SYNTHETIC STUDIES OF SOME COMPOUNDS CONTAINING N-N BONDS

BY

MOHAMMED MAHMOUD AL-SUBU

A DISSERTATION PRESENTED TO THE GRADUATE COUNCIL
OF THE UNIVERSITY OF FLORIDA IN
PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

1984

TO AMAL

ACKNOWLEDGEMENTS

I am deeply grateful to Professor Harry H. Sisler for his enthusiastic support and patience while the present work was in progress. Under his guidance and his example, my outlook on nonmetal chemistry in general and on nitrogen chemistry in particular has broadened considerably. The spirit of uninhibited inquiry present in his laboratory has been a source of inspiration for me.

I wish to recognize the friendly assistance, moral support and valuable comments of Professor George E. Ryschkewitsch, Professor Francis E. Dunnam, Professor George B. Butler, and Professor Willis B. Person.

Professor Wallace S. Brey has been of special assistance in obtaining and interpreting nuclear magnetic resonance spectra for this work.

I owe a special debt of thanks to Professor Robert M. Kren and Mr. Awni A. Khatib for the many discussions and ideas shared during the course of this work.

Thanks are also extended to my colleagues, Mr. Ismael L. Scott for obtaining the Raman spectra, Mr. Roy J. Vaz and Dr. Shadpour Mallakpour for their assistance in the study of the polymerization of 2,2-diallyltriazanium chloride.

I wish to thank Mrs. Laura E. Griggs for her patience and care in typing this dissertation.

I gratefully acknowledge the support of my study in the United States by the America-Mideast Educational and Training Services, Inc.

Finally, I wish to express my gratitude to my wife Amal, my children, my brother Abdelrahim, and all my family for their many personal sacrifices. Without their encouragement this work would not have been possible.

TABLE OF CONTENTS

		Page
ACKNOWLEDGEMENTS		iii
ABSTRACT		viii
INTRODUCTION		1
CHAPTER ONE	A STUDY OF THE REACTIONS OF DINITROGEN TETROXIDE WITH SOME CROWN ETHERS AND OTHER ALICYCLIC BASES...	3
	Introduction	3
	Historical Background	4
	Physical Constants	4
	Structure of Dinitrogen Tetroxide	4
	Equilibrium in Liquid and Gaseous Dinitrogen Tetroxide	7
	Solubilities in Liquid Dinitrogen Tetroxide..	9
	Acid-base Reactions	9
	Solvolytic Reactions	10
	Reaction with Metals	11
	Compound Formation with Electron Donors	11
	Compounds with Tertiary Amines and Similar Systems	12
	Compounds with Nitriles and Ketones	12
	Compounds with Organic Sulfides	13
	Structure of Addition Compounds with Bases...	13
	Experimental	14
	Materials	15
	Analyses	15
	Infrared Spectra	17
	Nuclear Magnetic Resonance Spectra	17
	Procedure	17
	Reactions of 1,4-Thioxane with Dinitrogen Tetroxide	27
	Reaction of N-Methylmorpholine with Dinitrogen Tetroxide	29
	Reactions of N,N'-dimethylpiperazine with Dinitrogen Tetroxide	38
	Reactions of Triethylenediamine with Dinitrogen Tetroxide	47

Page

Reactions of 12-Crown-4 Ether with Dinitrogen Tetroxide..... 50
Reactions of 15-Crown-5 Ether with Dinitrogen Tetroxide..... 55
Reactions of 18-Crown-6 Ether with Dinitrogen Tetroxide..... 55
Reactions of Dicyclohexyl-18-Crown-6 Ether with Dinitrogen Tetroxide..... 56
Reactions of Dicyclohexyl-24-Crown-8 Ether with Dinitrogen Tetroxide..... 56
Reactions of Dibenzo-18-Crown-6 Ether with Dinitrogen Tetroxide..... 59

Discussion and Conclusions..... 62

The Reaction with 1,4-Thioxane..... 62
The Reactions with Nitrogen Bases..... 70
Reactions with Crown Ethers..... 73

Summary..... 77

CHAPTER TWO A STUDY OF CHLORAMINATION OF DI- AND TRI-ALLYLAMINES..... 80

Introduction..... 80

Historical Background..... 81

Preparation in Aqueous Solution..... 81
Preparation in Gas Phase..... 81
Chemical Reactions..... 82

Experimental..... 85

Analyses..... 87
Infrared Spectra..... 87
Nuclear Magnetic Resonance Spectra..... 89
Mass Spectra..... 89
Reactions of the Chloramine-Ammonia Mixture with Diallylamine..... 89
Reactions of the Chloramine-Ammonia Mixture with Triallylamine..... 111
Polymerization of 2,2-Diallyltriazanium Chloride..... 113

Discussion and Conclusions..... 129

Summary..... 139

CHAPTER THREE A STUDY OF THE EFFECT OF 18-CROWN-6 ETHER ON THE CHLORAMINATION OF 1,1-DIMETHYLHYDRAZINE..... 141

Introduction..... 141

Historical Background..... 142

Methods of Synthesizing Triazanium Salts..... 140
Structure and Stability..... 144
Thermochemical Properties..... 145

Page

Experimental..... 145

Materials..... 145
Analyses..... 146
Nuclear Magnetic Resonance Spectra..... 148
The Reaction of 1,1-Dimethylhydrazine with Chloramine in the Presence of the Crown Ether 18-Crown-6..... 148
The Interaction of 18-Crown-6 Ether with Monomethylchloramine and Dimethylchloramine 150
18-Crown-6 Chloramine Adduct as Aminating Reagent for Triethylamine..... 158

Discussion and Conclusions..... 159

Summary..... 169

CHAPTER FOUR A STUDY OF THE COMPLEXES OF SOME CROWN ETHERS WITH ACETONITRILE..... 171

Introduction..... 171

Historical Background..... 174

Classification and Nomenclature of Crown Compounds..... 174
Synthesis and Properties of Crown Ethers..... 175
Characteristics of Crown Ethers..... 176

Experimental..... 178

Materials..... 178
Analyses..... 178
Infrared Spectra..... 178
Nuclear Magnetic Resonance Spectra..... 178
The Interaction of 18-Crown-6 Ether with Acetonitrile..... 184
The Interaction of Dicyclohexyl-18-crown-6 Ether with Acetonitrile..... 189
The Interaction of Dibenzo-18-crown-6 Ether with Acetonitrile..... 196

Discussion and Conclusions..... 196

Summary..... 205

CHAPTER FIVE CONCLUSIONS..... 207

REFERENCES..... 209

BIOGRAPHICAL SKETCH..... 216

Abstract of Dissertation Presented to the Graduate Council of the University of Florida in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

SYNTHETIC STUDIES OF SOME
COMPOUNDS CONTAINING N-N BONDS

By

Mohammed Mahmoud Al-Subu

December 1984

Chairman: Professor Harry H. Sisler
Major Department: Chemistry

The reactions of dinitrogen tetroxide with some crown ethers, either pure or in solution, and with some other alicyclic compounds containing one or more atoms of sulfur, nitrogen and/or oxygen were carried out. The products were analyzed and identified by available experimental methods such as infrared spectroscopy and nuclear magnetic resonance. The results show that (1) dinitrogen tetroxide reacts with aliphatic crown ethers such as 18-crown-6 and 15-crown-5 ethers to form 1:1 and 1:2 complexes, depending on the size of the crown ether cavity, whereas it nitrates the benzo units in dibenzo-18-crown-6 ether to give the cis- isomer of the dinitro derivative; (2) in the alicyclic compounds studied, dinitrogen tetroxide oxidizes the sulfur atom to the corresponding S-oxide as, for example, in 1,4-thioxane, and it oxidizes the one or the two nitrogen atoms to give the corresponding N-oxide or N,N'-dioxide as in N-methylmorpholine and N,N'-dimethylpiperazine, respectively. The resulting N-oxide or N,N'-dioxide reacts further to form a complex with N_2O_4.

The chloramination of diallylamine and triallylamine by chloramine was also studied, and the products of the reactions were identified by several methods. The data show that chloramine reacts with di- and triallylamine to give 2,2-diallyltriazanium chloride and 1,1,1-triallylhydrazinium chloride, respectively. The former chloride was polymerized in aqueous solutions via a free radical initiated mechanism, and a high yield of a cross-linked solid polymer was obtained.

The third study was the reaction of 1,1-dimethylhydrazine with an etheral solution of chloramine in the presence of 18-crown-6 ether. It was shown that the presence of 18-crown-6 ether greatly improves the yield of 2,2-dimethyltriazanium chloride. It was also shown that 18-crown-6 ether forms a 1:1 adduct with chloramine. Further, this adduct acts as a chloraminating agent toward triethylamine to give 1,1,1-triethylhydrazinium chloride.

Finally, it was shown that the interaction of acetonitrile with 18-crown-6 ether and dicyclohexyl-18-crown-6 ether results in the formation of adducts or complexes, which was shown by the experimental data to contain two moles of acetonitrile per mole of the crown ether. Further, of the two isomers of dicyclohexyl-18-crown-6 ether studied in the present work, only one is capable of forming a stable adduct with acetonitrile. This behavior was used to separate a mixture of the two isomers of dicyclohexyl-18-crown-6 ether, viz. cis-anti-cis and cis-syn-cis.

INTRODUCTION

The studies that form the subject matter of this dissertation had their inception in a series of conversations between the author and Professor Harry H. Sisler of the University of Florida Department of Chemistry concerning the chemistry of high-energy nitrogen compounds, such as hydrazines and triazanium salts, containing nitrogen in lower oxidation states, and high-energy compounds, such as dinitrogen tetroxide, containing nitrogen in higher oxidation states. These conversations led to a consideration of various methods for incorporating these high-energy compounds into solid phases possibly suitable for blending into solid rocket fuels. The research that has resulted from these considerations and which is encompassed by this dissertation has proceeded along four pathways that are discussed in the four chapters that follow:

I. The Reactions of Dinitrogen Tetroxide with Some Crown Ethers and Other Alicyclic Bases.

II. The Chloramination of Di- and Triallylamines.

III. The Effect of 18-Crown-6 Ether on the Chloramination of 1,1-Dimethylhydrazine.

IV. Complexes of Some Crown Ethers with Acetonitrile.

In the first study, a number of solid adducts of dinitrogen tetroxide were isolated from the interaction of dinitrogen tetroxide with a variety of crown ethers and were characterized. In the second study, di- and triallylamines were converted to 2,2-diallyltriazanium chloride and 1,1,1-triallylhydrazinium chloride, respectively, by reaction with

chloramine. The former in turn was polymerized to yield a solid phase containing the high-energy group $[N-\overset{|}{N}-N-]^+$, distributed along polymeric hydrocarbon chains. In the third study, it was shown that the presence of 18-crown-6 ether greatly improves the yield of 2,2-dimethyltriazanium chloride from the chloramination of 1,1-dimethylhydrazine. It was also shown that the 18-crown-6 ether forms a solid adduct with chloramine, and that this adduct acts as a chloraminating agent. Finally, in the fourth study, some new chemistry of adducts of some crown ethers with acetonitrile was discovered. It was found that such adduct formation with acetonitrile provides a method for separating geometric isomers of certain crown ethers.

It should be noted that the historical background concerning the crown ethers and relating to Chapters 1, 3 and 4 is placed in Chapter 4. The historical background concerning chloramine is placed principally in Chapter 2 except for that relating to the formation of triazanium chlorides which is to be found in Chapter 3. This arrangement made possible considerable economy in space.

CHAPTER ONE

A STUDY OF THE REACTIONS OF DINITROGEN TETROXIDE WITH SOME CROWN ETHERS AND OTHER ALICYCLIC BASES

Introduction

Studies in this laboratory of the reactions of dinitrogen tetroxide with a variety of electron donor ether systems have shown that 1,4-dioxane reacts with dinitrogen tetroxide to form an addition compound with properties strikingly different from those of addition compounds of monobasic ethers. It was shown that 1,4-dioxane forms an adduct with a different mole ratio and strikingly different stability. The dinitrogen tetroxide-1,4-dioxane adduct melts at 45.2°C whereas the dinitrogen tetroxide-2 ethyl ether adduct melts at -74.8°C. This was explained by the assumption of a tricyclic structure in which the two oxygens of the dioxane molecule each share a pair of electrons with the same dinitrogen tetroxide molecule.[1]

It was thought that the reactions of dinitrogen tetroxide with alicyclic substances containing more than two basic oxygen centers, such as crown ethers, might result in solid adducts of even higher stability. A crown ether would provide several possibilities of reactions depending on several factors; these factors include the relative sizes of the dinitrogen tetroxide molecule and the cavity in the crown ether ring, and the number, basicity, coplanarity, and symmetrical placement of the oxygen atoms in the crown ether.

This study was conducted to determine how dinitrogen tetroxide interacts with crown ethers and other alicyclic bases containing two nitrogen atoms, a nitrogen atom and an oxygen atom, and an oxygen atom and a sulfur atom, to determine the nature of the reaction products and to examine the possibility of the existence of molecular and ionic addition compounds.

Historical Background

Physical Constants

Dinitrogen tetroxide melts at -12.3°C (the triple point is at -11.2°C), and its normal boiling point is 21.3°C. The liquid may be supercooled and has been cooled as low as -110°C without crystallizing. Its critical temperature is 158.2°C, and its critical pressure is 100.0 atm. The density of dinitrogen tetroxide is 1.49 g/cc at 0°C. The specific conductance at various temperatures expressed in $ohm^{-1}\ cm^{-1}$ is given by the equation $\log K = (-1267/T) - 8.260$. This corresponds to a value for K of $2.36 \times 10^{-13}\ ohm^{-1}\ cm^{-1}$ at 17°C.

Structure of Dinitrogen Tetroxide

The structure of dinitrogen tetroxide has been extensively investigated by x-ray diffraction and electron diffraction[2-6] with results which may be summarized as follows: Pure N_2O_4 in the solid state at not-too-low temperatures and in the liquid and the gaseous states consists of coplanar molecules of D_{2h} symmetry having the configuration $O_2N\text{-}NO_2$ as shown in Figure 1.1. Values for the structural parameters of the D_{2h} symmetry species have been obtained from x-ray crystallographic and gas electron-diffraction investigations and are shown in Table 1.1.

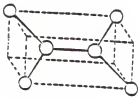


Figure 1.1. N_2O_4 geometry.

Table 1.1

Geometry of N_2O_4 Determined from Several Investigations

Structural Parameters	Broadley and Robertson[2]	Smith and Hedberg[3]	Groth[4]	Cartwright and Robertson[5]	McClelland et al.[6]
r_{N-N} (Å)	1.64	1.750	1.75	1.745	1.782
r_{N-O} (Å)	1.17	1.180	1.21	1.214	1.190
∠ONO (deg)	126	133.7	135	133.7	135.4

It has been found from x-ray crystallography that both the N-N and N-O bonds in D_{2h} N_2O_4 are sensitive to temperature;[5] they increase in length about 0.01 Å per 100K of temperature rise. However, no significant change in the ONO angle was found.

The existence of molecules with the same configuration but staggered (symmetry D_{2d}) has been reported in solid N_2O_4 at liquid nitrogen temperatures[7] (see Figure 1.2).

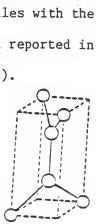


Figure 1.2. Geometry of N_2O_4 (D_{2d} symmetry) at liquid nitrogen temperatures.

There also is evidence for the existence of the unsymmetrical molecule $ONO{\cdot}NO_2$ (see Figure 1.3) in argon matrices at liquid helium

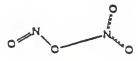


Figure 1.3. Proposed structure of iso-N_2O_4.

temperatures.[7] However, recent electric deflection measurement of beams of NO_2-N_2O_4 system[8] showed extensive polymerization beyond that of a dimer. Equilibrium constants measurements imply that the reaction $NO_2 + N_2O_4 \overset{k}{\rightleftharpoons} N_3O_6$ is exothermic by approximately 4 kcal mol^{-1}. Thus, it is speculated that iso-N_2O_4 is in fact a trimer (N_3O_6) which is very similar in local symmetry to the proposed structure of iso-N_2O_4 (see Figure 1.4).

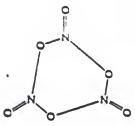


Figure 1.4. Proposed structure of NO_2 trimer.

The most peculiar features of the dinitrogen tetroxide structure are (1) an unusually long, weak N-N bond with a bond distance of 1.78 Å, whereas the N-N bond distance in N_2H_4 is only 1.47 Å, and (2) coplanarity of the molecule. Here briefly are some attempts that have been made to explain the geometry of N_2O_4.

Smith and Hedberg[3] have noted that the long N-N distance could be explained by assuming a "π-only" bond, with no σ bond between the NO_2 fragments at all. This would explain the planarity of N_2O_4.

Pauling[9] has rejected this explanation by the following reasoning. The unpaired electron in NO_2 clearly occupies a σ MO, and consequently a σ bond should be formed. As the odd electron in NO_2 is delocalized and is located only 42% on the nitrogen atom,[9] one would expect a bond strength of 0.42 which corresponds to a bond length of about 1.75 Å, but Pauling did not attempt to give an explanation of the planarity of N_2O_4.

Ahlrichs and Keil[10] proved definitely the σ character of the N-N bond by ab initio computations and showed that the very long N-N bond in N_2O_4 is due to the delocalization of the bond electron pair over the whole molecule and to a rather large repulsion between the doubly occupied MO's of the NO_2 fragments. The coplanarity of N_2O_4 results from a delicate balance of the repulsive forces, which favor the staggered structure, and the effects of bonding which favor the planar structure.

Equilibrium in Liquid and Gaseous Dinitrogen Tetroxide

In both the liquid and gaseous states, dinitrogen tetroxide is in mobile equilibrium with the brown, paramagentic monomeric species NO_2, nitrogen dioxide. The change in equilibrium with change in temperature may be readily followed spectrophotometrically, tensimetrically, or by measuring the magnetic susceptibility. The equilibrium constants and enthalpies for the reaction

$$N_2O_4 \rightleftharpoons 2NO_2$$

have been measured in both coordinating and non-coordinating solvents by the NMR method.[11] Thermodynamic values for the N_2O_4 dissociation in

Table 1.2

Thermodynamic Values for N_2O_4 Dissociation

Solvent	K_c^{298}	ΔF_{dissn}^{298} kcal mol^{-1}	ΔH_{dissn}^{298} kcal mol^{-1}	ΔS_{dissn}^{298} eu
Cyclohexane	1.77×10^{-4}	5.1	14.6	31.8
Carbon tetrachloride	1.78×10^{-4}	5.1	14.6	31.8
Acetonitrile	0.3×10^{-4}	6.1	16	33.0
Gas phase	1.51×10^{-1}	1.12	13.68	42.8

these solvents and in the gas phase are shown in Table 1.2. The extent of dissociation of N_2O_4 in non-coordinating solvent is clearly much less than in the gas phase, and that must result primarily from a much lower entropy change in the liquid phase. The increase in association of N_2O_4 in coordinating solvents suggests that N_2O_4 is a better Lewis acid than NO_2 and thus is more highly associated with acetonitrile than is NO_2.

Dinitrogen tetroxide undergoes self-ionization according to the equation

$$N_2O_4 \longrightarrow NO^+ + NO_3^-$$

The concentrations of nitrosonium (NO^+) and nitrate (NO_3^+) ions in the pure liquid are extremely low, and their presence is very difficult to detect. However, a demonstration that some nitrate ions must be present has come from exchange studies using the ^{15}N isotope.[12] Complete exchange of ^{15}N is observed in a solution of tetramethylammonium nitrate $[(CH_3)_4N]^+[^{15}NO_3]^-$ in liquid dinitrogen tetroxide. Self

ionization of N_2O_4 is enhanaced by dissolving N_2O_4 in solvents of high dielectric constant, e.g., nitromethane, nitric acid, sulfuric acid, etc.

Different products are obtained when BF_3 reacts with pure N_2O_4; these have the stoichiometry $N_2O_4 \cdot BF_3$ and $N_2O_4 \cdot 2BF_3$ and are formulated as ionic compounds $[NO_2]^+[BF_3NO_2]^-$ and $[NO_2]^+[N(OBF_3)_2]^-$, respectively. These reactions suggest that ionization of N_2O_4 has occurred according to

$$N_2O_4 \rightleftharpoons NO_2^+ + NO_2^-$$

Solubilities in Liquid Dinitrogen Tetroxide

Few inorganic salts are soluble in dinitrogen tetroxide, and in some ways solubilities in N_2O_4 resemble those in nonpolar organic solvents like benzene. Non-metallic elements like bromine and iodine dissolve freely in N_2O_4, and N_2O_4 is miscible with covalent inorganic compounds like CS_2 and $SiCl_4$.

Many organic compounds like alkanes, aromatic hydrocarbons, halo- and nitro-hydrocarbons, and carboxylic acids dissolve readily in N_2O_4 without reaction and may be recrystallized using N_2O_4 as a solvent. Dinitrogen tetroxide forms addition compounds with amines, heterocyclic nitrogen and oxygen compounds, ethers, nitriles, and ketones. Alkenes, alcohols, many amines, and some ketones react with dinitrogen tetroxide.

The strong oxidizing tendency of N_2O_4 prevents its use as a solvent for many solutes with reducing properties.

Acid-base Reactions[13]

The dissociation equilibrium mentioned above

$$N_2O_4 \rightleftharpoons NO^+ + NO_3^-$$

may be considered to be analogous to autoionization reactions known for water

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

According to this point of view, substances furninshing the NO^+ group, e.g. NOCl, would be typical acids in dinitrogen tetroxide, and substances furnishing NO_3^- ions, e.g. $AgNO_3$, would be typical bases. A solution of NOCl in liquid dinitrogen tetroxide reacts with solid silver nitrate.

$$NOCl + AgNO_{3(s)} \xrightarrow[N_2O_4]{\text{liquid}} AgCl_{(s)} + N_2O_4$$

The reaction would be a typical neutralization reaction analogous to the following reaction from the water system:

$$(H_3O)Cl + NaOH \xrightarrow{H_2O} NaCl + 2H_2O$$

Solvolytic Reactions

A number of solvolytic reactions in liquid dinitrogen tetroxide have been investigated. The general type of reaction

$$MCl + N_2O_4 \longrightarrow NOCl + MNO_3$$

is fully reversible in liquid N_2O_4, depending upon the solubility of MCl and the removal of NOCl from the system.

$$KCl_{(\text{slightly moist})} + N_2O_4 \longrightarrow NOCl + KNO_3$$

Other solvolytic reactions include the following:

$$[Mg(H_2O)_6]Cl_2 + 2N_2O_4 \longrightarrow [Mg(H_2O)_6](NO_3)_2 + 2NOCl$$

$$2AlCl_3 + 7N_2O_4 \longrightarrow Al(NO_3)_3 + NO[Al(NO_3)_4] + 6NOCl$$

$$Li_2CO_3 + 2N_2O_4 \longrightarrow 2LiNO_3 + N_2O_3 + CO_2$$

Liquid dinitrogen tetroxide likewise reacts with calcium oxide, calcium carbonate, sodium hydroxide, zinc carbonate, and zinc sulfide to give anhydrous nitrates, sometimes mixed with nitrites. The reactions are slow but may be accelerated by adding traces of water, still obtaining essentially an anhydrous nitrate product.

Reaction with Metals[14-18]

Very active metals react with liquid dinitrogen tetroxide in a manner analogous to their reactions with water.

$$M_{(s)} + N_2O_{4(l)} \longrightarrow NO + MNO_3 \qquad (M = \text{alkali metal})$$

$$M_{(s)} + H_2O_{(l)} \longrightarrow \tfrac{1}{2}H_2 + MOH$$

Addition of NOCl to liquid dinitrogen tetroxide increases its reactivity toward metals.

$$M_{(s)} + 2NOCl \xrightarrow[N_2O_4]{liq} MCl_2 + 2NO \qquad (M = An, Fe, Sn, etc.)$$

Tin(IV) chloride is an exception among metal chlorides in that it does not undergo solvolysis in dinitrogen tetroxide at room temperature but forms a fairly stable adduct of variable $SnCl_4/N_2O_4$ stoichiometry.[15]

Complexes of metals with d^8 and d^{10} electronic configuration undergo oxidative addition reactions to form complexes of metals with d^6 and d^8 electronic configuration.[18]

$$M + \tfrac{3}{2}N_2O_4 \longrightarrow [M(NO_2)(ONO_2)] + NO$$

Compound Formation with Electron Donors

Compound formation has been reported in liquid mixtures of dinitrogen tetroxide with a variety of electron-donor substances.[19-26] They have been investigated by the classical methods of cryoscopy, conductivity, viscosity, etc.; no structural determinations have been completed.

Addition compounds of the type $N_2O_4 \cdot 2B$, where B represents the base, have been observed between dinitrogen tetroxide and ethers and other oxygen derivatives.[25,26] Melting points and phase diagrams are recorded. With diethers such as dioxane or ethylene glycol diethyl ether, the general formula is $N_2O_4 \cdot B$.[24-26]

Perfluorotetrahydrofuran and di-tert-butyl ether fail to give addition compounds.[26] It is suggested that the electron density at the oxygen atom of the former is too low, owing to the electron withdrawing effect of the eight fluorine atoms,[26] and that the two four-carbon groups of the latter are too bulky, although the electron distribution should be suitable.

Compounds with Tertiary Amines and Similar Systems

Compounds of the general formula $N_2O_4 \cdot B$ and $N_2O_4 \cdot 2B$ are also formed with tertiary amines.[27,28] They are stable only at low temperatures. All the bases studied form compounds of the type $N_2O_4 \cdot 2B$; the species $N_2O_4 \cdot B$ has not been found for all.

Compounds which do not give such addition compounds with dinitrogen tetroxide are o-, m- and p-nitrodimethylaniline; α,α'-lutidine; and 2-methylquinoline.[29] Steric hindrance has been proposed as the factor preventing compound formation by these three heterocyclic compounds.

Compounds with Nitriles and Ketones

Acetonitrile and benzonitrile also form addition compounds.[21] Acetonitrile forms both $N_2O_4 \cdot CH_3CN$ and $N_2O_4 \cdot 2CH_3CN$, whereas benzonitrile yields only $N_2O_4 \cdot C_6H_5CN$.

Acetone reacts with liquid dinitrogen tetroxide at low temperatures, yielding a complex mixture of reaction products among which cyanides, nitrates, and nitro compounds have been found. At low temperatures (-40°C), however, the compound $N_2O_4 \cdot 2(CH_3)_2CO$ is formed.[22]

Compounds with Organic Sulfides

Dinitrogen tetroxide oxidizes organic sulfides to the corresponding sulfoxides.[30-32] Addition compounds between dinitrogen tetroxide and sulfoxides have also been investigated, and it has been suggested that the formation of these compounds may inhibit further oxidation of the sulfur atom to the sulfones.

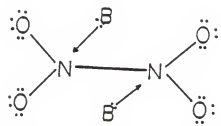
Structure of Addition Compounds with Bases[16]

It is believed that binary systems composed of dinitrogen tetroxide and an electron donor species involve the equilibrium

$$\underset{\text{ionic}}{[(B)_n NO]^+[NO_3]^-} \rightleftharpoons nB + N_2O_4 \rightleftharpoons \underset{\text{molecular}}{N_2O_4 \cdot nB}$$

where B is a very strong electron donor, the equilibrium will be shifted to the left, and an ionic complex will be obtained. For very weak electron donors, the equilibrium will be shifted to the right and molecular complexes will be formed.

The molecular structure can be indicated as



and the ionic structure involves the sharing of electrons from the donor molecule with nitrosylium ion NO^+.

(a) $[B:\longrightarrow N{=}O:^+][NO_3^-]$ or

(b) $[B:\longrightarrow \underset{\uparrow}{\underset{B}{N}}{-}O:^+][NO_3^-]$

Experimental

In this chapter the interactions of the following compounds 1 through 10 with N_2O_4 are described.

1

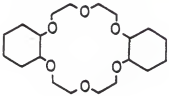
12-crown-4 ether

2

15-crown-5 ether

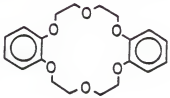
3

18-crown-6 ether



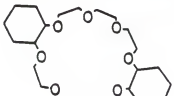
4

dicyclohexyl-18-crown-6 ether



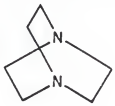
5

dibenzo-18-crown-6 ether



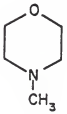
6

dicyclohexyl-24-crown-8 ether



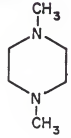
7

1,4-diazabicyclo [2·2·2] octane



8

n-methymorpholine



9

n,n'-dimethylpiperazine

10

1,4-thioxane

Materials

The following chemicals were used in this study: carbon tetrachloride, phosphorus pentoxide (Fisher, ACS reagent), chlorobenzene (Mallinkrodt, AR analytical reagent), absolute ethanol (Florida Distiller's Co., USP 200 proof), anhydrous diethyl ether (Fisher, laboratory grade), sand (Mallinkrodt). Compounds 1 (99%), 2, 3 (99%), 4 (98%), 5 (99%), 6 (97%), 7 (97%), 8 (99%), 9 (98%) and 10 (98%) were all obtained in the best available purity from Aldrich Chemical Co., and used without further purification.

Dinitrogen tetroxide was prepared by condensation of commercial nitrogen dioxide (Matheson Co.) and purified in an all-glass apparatus shown in Figure 1.5. The gas was condensed in the first trap at dry ice-acetone temperature. The solid was then melted and kept at 0°C while dry oxygen was bubbled through the liquid until the color had changed to orange-red. The liquid was further purified by passing it, at room temperature, through the two glass tubes containing a mixture of sand and phosphorus pentoxide. Solid dinitrogen tetroxide was then collected in the second trap cooled by dry ice-acetone mixture and stored at the same temperature until needed. Purity of the dinitrogen tetroxide was attested by its snow white color in the solid state.

Analyses

Elemental analyses were done by Galbraith Laboratories, Inc., Knoxville, Tennessee. Melting points were obtained in sealed capillary tubes in a Thomas Hoover capillary melting point apparatus and are reported uncorrected.

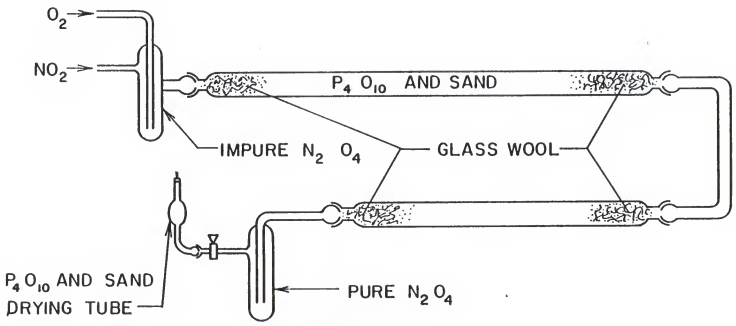


Figure 1.5. Dinitrogen tetroxide purification apparatus.

Infrared Spectra

Infrared (IR) spectra were recorded on a Perkin-Elmer 283B infrared spectrophotometer. Solid samples were examined as KBr pellets or as Nujol mulls using sodium chloride plates. Liquid samples were examined neat between salt plates. A summary of the IR data is found in Table 1.3.

Nuclear Magnetic Resonance Spectra

Nuclear magnetic resonance (NMR) spectra were recorded on a Varian EM 360L NMR spectrometer or Nicolet 300 MHz multinuclear Fourier-Transform NMR spectrometer. Appropriate solvents were used with trimethylsilane (TMS) as a reference. The NMR spectral data are listed in Table 1.4.

Procedure

The reactions of dinitrogen tetroxide with the various cyclic compounds were carried out in an atmosphere of prepurified nitrogen in an all-glass apparatus that was fitted with Teflon plug stopcocks and Teflon sleeve joints. All ball joints were lubricated using fluorocarbon grease. A diagram of the reaction apparatus is shown in Figure 1.6. A weighed sample of the cyclic base was placed in flask A, either neat or in the presence of the proper solvent, and an excess of dinitrogen tetroxide condensed over it from transfer cell B through a 20 cm tube packed with a mixture of phosphorus(V) oxide and sand. The reflux condenser was kept at temperatures between 0°C and -78°C to prevent the escape of dinitrogen tetroxide during the reaction period. Occasional stirring was provided by a Teflon coated magnetic stirring bar. At the end of the reaction period, the excess dinitrogen tetroxide was removed through trap D at room temperature using a stream of nitrogen gas. All

Table 1.3

Infrared Absorption in cm^{-1} [a]

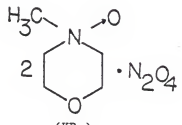
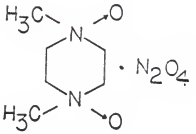
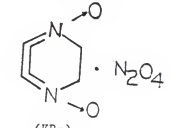
1,4-thioxane 4-oxide (KBr)	2960 (m), 2920 (m), 2760 (s), 1910 (w), 1610 (vw), 1500 (vw), 1460 (s), 1400 (s,mb), 1315 (w), 1270 (s), 1285 (m,sh), 1210 (s), 1190 (w), 1150 (w), 1140 (m), 1095 (vs), 1055 (d,vs), 1010 (d,vs), 990 (d,m), 955 (m), 825 (vs), 695 (m), 660 (m), 555 (m), 430 (vs)
 (KBr)	3020 (vw), 2940 (mb,m), 2880 (sh,m), 2690 (s), 2600 (sh,m), 2470 (m), 1765 (w), 1460 (sh,s), 1440-1320 (b,s), 1310 (sh,w), 1275 (m), 1200 (d,s), 1115 (vs), 1090 (sh,s), 1050 (m), 1035 (s), 1020 (m), 990 (s), 890 (s), 865 (vs), 825 (s), 605 (s)
 (KBr)	3020 (d,m), 2700 (b,m), 2460 (b,m), 1795 (w), 1755 (w), 1740 (m), 1670 (w), 1655 (m), 1470 (mb,s), 1370 (mb,s), 1270 (mb,s), 1160 (w), 1135 (s), 1065 (d,s), 1037 (s), 935 (s), 890 (s), 830 (w), 815 (vs), 710 (s), 700 (w), 603 (m), 565 (m), 445 (s)
 (KBr)	3100-2900 (b,s), 2850-2750 (b,s), 2700-2500 (b,s), 2500-2000 (sh,m), 1760 (m), 1470 (mb,s), 1450-1250 (b,vs), 1220 (b,s), 1050 (d,vs), 975 (s), 950 (sh,w), 890 (v,w), 860 (m), 850 (sh,m), 840 (s), 815 (s), 715 (s), 705 (sh,vw), 600 (vw)

Table 1.3--continued

18-crown-6 ether•N_2O_4 (Nujol)	2900 (s), 2730 (w), 2675 (vw), 1800 (s), 1470-1440 (mb,vs), 1380-1350 (mb,vs), 1300 (vw), 1150-1100 (mb,s), 960 (b,s), 890 (vw), 835 (w), 735 (sh,m), 725 (d,s)
Dinitrodibenzo-18-crown-6 ether (KBr)	3140-3040 (mb,w), 2890-2820 (mb,m), 1735 (w), 1710 (vw), 1680 (w), 1590 (d,s), 1510 (d,vs), 1450 (w), 1340 (d,vs), 1275 (vs), 1235 (sh,w), 1135 (s), 1095 (sh,s), 1070-1015 (mb,m), 1000 (w), 985-940 (mb,m), 895 (w), 875 (w), 865 (w), 805 (s), 745 (s), 720 (sh,w), 645 (m).
Dicyclohexyl-18-crown-6 ether•N_2O_4 (Nujol)	2960-2890 (b,vs), 2850 (sh,s), 1795 (m), 1610 (b,w), 1470-1430 (mb,s), 1375 (vs), 1245 (vw), 1195 (vw), 1155 (sh,w), 1125 (sh,m), 1095 (vs), 1080 (sh,s), 990 (s), 930 (vw), 905 (vw), 880 (vw), 845 (vw), 820 (vw), 805 (w)
Dicyclohexyl-24-crown-6 ether•N_2O_4 (Nujol)	2980-2840 (mb,vs), 1800 (w), 1720 (b,w), 1470-1435 (mb,vs), 1385-1320 (mb,vs), 1250 (vw), 1150-1010 (b,s), 990 (vw), 920 (b,w), 800 (b,w), 720 (w)

a b, Broad; d, doublet; m, medium; mb, multiple bands; s, strong; sh, shoulder; v, very; w, weak.

Table 1.4

Nuclear Magnetic Resonance Data[a]

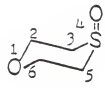
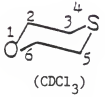
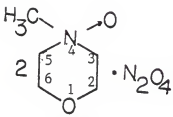
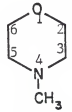
Compound	δ (ppm)	Assignment	^{1}H NMR J (Hz)
	4.364 (m)	H-2A,H-6A	$J_{2A,2E} = J_{6A,6E} = 12.76$
			$J_{2A,3A} = J_{6A,5A} = 9.90$
			$J_{2A,3E} = J_{6A,5E} = 2.13$
($CDCl_3$)	3.828 (m)	H-2E,H-6E	$J_{2E,3A} = J_{6E,5A} = 3.87$
	2.956 (m)	H-3A,H-5A	$J_{3A,3E} = J_{5A,5E} = 13.29$
	2.744 (m)	H-3E,H-5E	$J_{3E,2E} = 4.26$
	4.04 (t)	H-2,H-6	
($CDCl_3$)	2.68 (t)	H-3,H-5	
	2.982 (s)	$-CH_3$	
($CDCl_3$)	3.148 3.549	H-3,H-5	
	3.921 4.047	H-2,H-6	
	2.28	$-CH_3$	
	2.39	H-3,H-5	
($CDCl_3$)	3.69	H-2,H-6	

Table 1.4--extended

^{1}H NMR	^{13}C NMR		
Relative Area Ratio	δ (ppm)	Assignment	J (Hz)
1	59.127 (t)	C-2,C-6	J_{CH} = 138.54
	46.309 (t)	C-3,C-5	J_{CH} = 147.08
1			
1			
1			
1			
1			
3	44.023 (q)	$-CH_3$	J_{CH} = 143.03
4	53.737 (t)	C-3,C-5	J_{CH} = 144.37
4	63.930 (t)	C-2,C-6	J_{CH} = 146.77
3			
4			
4			

Table 1.4--continued

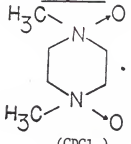
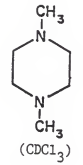
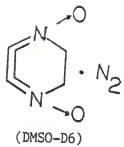
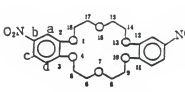
Compound	δ (ppm)	Assignment	J (Hz)	Relative Area Ratio
 (CDCl$_3$)	2.508 (s)	impurity		-
	2.865 (s)	-CH_3		3
	3.423 (b)	-CH_2		4
	3.780,3.916 4.483,4.537	impurities		-
 (CDCl$_3$)	2.33 (s)	-CH_3		3
	2.50 (s)	-CH_2		4
 (DMSO-D6)	3.665 (s)	-CH_2		6
	10.16 (b)	H_2O		1
(CDCl$_3$)	2.87 (s)			

Table 1.4--extended

^{13}C NMR

δ (ppm)	Assignment	J (Hz)
42.951	$-CH_3$	
50.341	$-CH_2$	
43.169		

Table 1.4--continued

Compound	δ (ppm)	Assignment	^{1}H NMR J (Hz)	Relative Area Ratio
	7.897 (q)	H_c	$J_{c,a}$ = 2.51	1
			$J_{c,d}$ = 8.94	
	7.727 (d)	H_a	$J_{a,c}$ = 2.56	1
(DMSO-D6) (21°C)	7.166 (d)	H_d	$J_{d,c}$ = 9.02	1
	4.219 (s)	H-5,-9,-14, -18		4
	3.869 (s)	H-6,-8,-15, -17		4

a s, Singlet; d, doublet; t, triplet; b, broad; m, multiplet; q, quartet; E, equatorial; A, axial.

Table 1.4--extended

^{13}C NMR

δ (ppm)	Assignment	J (Hz)
153.732	C-3,11	
147.641	C-2,12	
140.541	C-b	
117.606	C-c	
111.242	C-d	
106.544	C-a	
68.395	$-CH_2$	

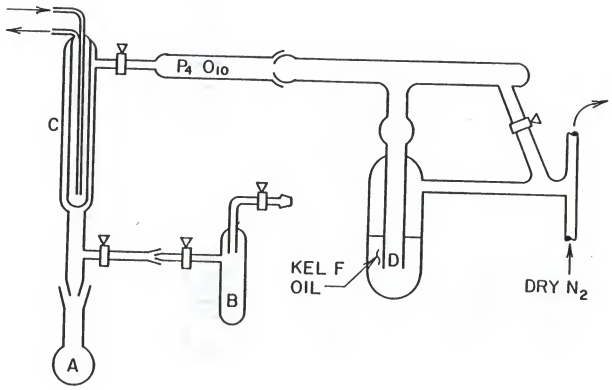


Figure 1.6. Reaction apparatus of dinitrogen tetroxide with the different bases.

filtrations were carried out under nitrogen atmosphere at -10°C using a low-temperature filtration apparatus (see Figure 1.7).

Reactions of 1,4-Thioxane with Dinitrogen Tetroxide

(1). A mixture of 0.01 mol of 1,4-thioxane (bp 147°C) and excess dinitrogen tetroxide was held at dry ice temperature for 90 min. As the temperature was allowed to rise to 0°C, reaction began even before the dinitrogen tetroxide was completely melted as indicated by gas evolution and a greenish colored liquid. After the removal of excess nitrogen oxides, the remaining solution was cooled by a water-ice mixture, and a white solid formed immediately. The deliquescent, odorless solid melted at 43°C, yield 1.3 g (94% of theory based on 1,4-thioxane used).

Anal. Calcd. for $\cdot H_2O$: C, 34.77; H, 7.30; O, 34.73; S, 23.20. Found: C, 35.30; H, 7.55; O, 34.20; S, 22.91.

(2). About 0.03 mol of 1,4-thioxane was dissolved in 35 mL of carbon tetrachloride. An excess of dinitrogen tetroxide was distilled into this solution, and the entire mixture held at 0°C for about 1 hr. At the end of this time, the system was composed of a blue-green solution. The excess oxides of nitrogen were removed over a 5 hr period, and large white crystals were deposited from the solution upon cooling to 0°C. These were removed, washed with a little diethyl ether and dried. The yield (3.2 g) based on 1,4-thioxane was 89%. The crystalline product was sublimed under vacuum and stored over phosphorus(V) oxide in a desiccator; the melting point was 46-47°C.

Anal. Calcd. for : C, 39.95; H, 6.71; O, 26.63; S, 26.68. Found: C, 39.80; H, 6.72; O, 26.84; S, 26.64.

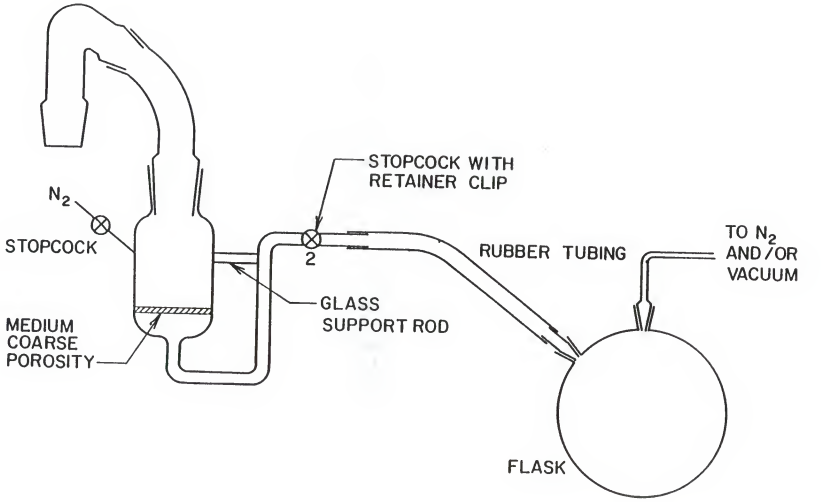


Figure 1.7. Apparatus for low temperature filtration.

The infrared spectrum of the product shows, in addition to bands due to 1,4-thioxane, a strong band at about 1550 cm^{-1} which is associated with the S=O bond as reported for sulfoxides of similar type.[33]

The ^{1}H NMR spectrum of the compound is given in Figure 1.8 (a,b). All peaks were resolved and analyzed; the coupling constants were calculated and documented in Table 1.4. The spectrum consists of four multiplets centered at 4.363, 3.828, 2.956 and 2.744 ppm and are assigned to the axial hydrogens at C-2 and -6, the equatorial hydrogens at C-2 and -6, the axial hydrogens at C-3 and -5, and the equatorial hydrogens at C-3 and -5, respectively. The ^{1}H NMR data for 1,4-thioxane are given in Table 1.2 for comparison.

The ^{13}C NMR spectrum [Figure 1.9 (a,b)] shows two peaks for the product: the peak at 59.127 ppm is a triplet (J_{CH} = 138.55 Hz) and is attributed to C-2 and -6; the second peak is also a triplet centered at 46.309 ppm (J_{CH} = 147.08) and is assigned to C-3 and -5.

Reaction of N-methylmorpholine with Dinitrogen Tetroxide

(1). A mixture of dinitrogen tetroxide and about 0.01 mol of N-methylmorpholine (bp 115-116°C) was allowed to react for 2 hr at -78°C and then warmed to room temperature. The brownish gum obtained after removal of nitrogen oxides was recrystallized from absolute ethyl alcohol. The product is a highly deliquescent yellowish crystals which were filtered, washed with diethyl ether, and dried in vacuo at room temperature for several hours. The weight of the dry solid (mp 75-77°C) was 1.4 g (87% of theory).

Anal. Calcd. for

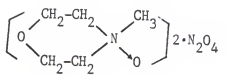


Figure 1.8. (a) The 300 MHz ^{1}H NMR spectrum of 1,4-thioxane 4-oxide in $CDCl_3$ solution.

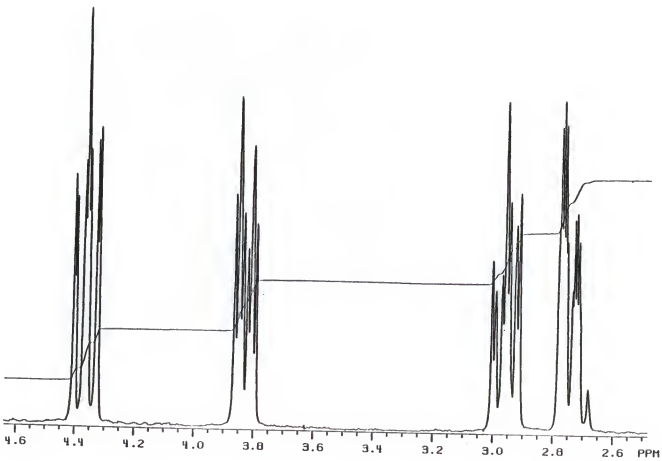
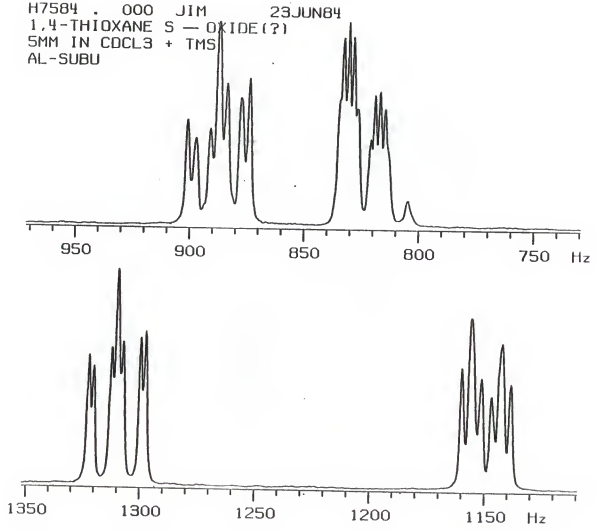

H7584 . 000 JIM 23JUN84
1,4-THIOXANE S - OXIDE(?)
5MM IN CDCL3 + TMS
AL-SUBU
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
PPM

Figure 1.8 (continued). (b) The ^{1}H NMR spectrum of 1,4-thioxane 4-oxide, with expansion.


H7584 . 000 JIM 23JUN84
1,4-THIOXANE S — OXIDE(?)
5MM IN CDCL3 + TMS
AL-SUBU
950
900
850
800
750 Hz
1350
1300
1250
1200
1150 Hz

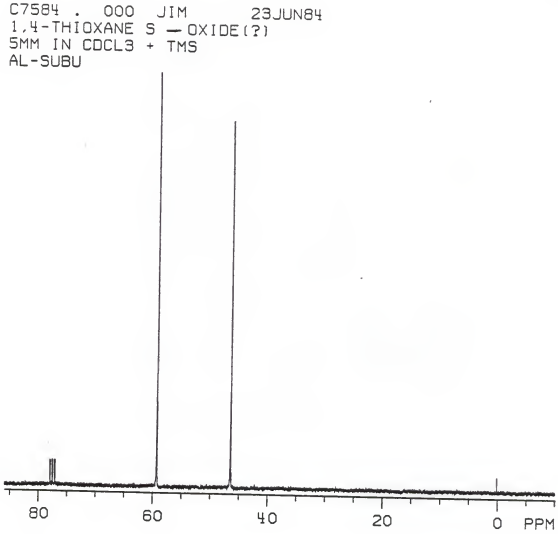
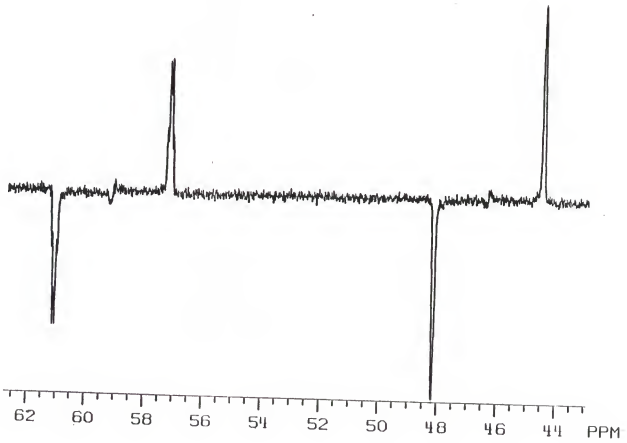


Figure 1.9. The 300 MHz ^{13}C NMR spectrum of 1,4-thioxane 4-oxide in $CDCl_3$ solution.
(a) Proton noise decoupled.

Figure 1.9 (continued). (b) The undecoupled ^{13}C NMR spectrum of 1,4-thioxane 4-oxide.

C7584 . 001 JIM 23JUN84
1,4-THIOXANE S — OXIDE(?)
5MM IN CDCL3 + TMS
AL-SUBU

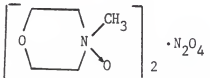


C, 36.81; H, 6.80; N, 17.17; O, 39.22. Found: C, 36.86; H, 7.02; N, 17.34; O,38.68.

However, when a considerable excess of dinitrogen tetroxide was used, ignition occurred even at very low temperatures.

(2). The same product was obtained by treating about 0.045 mol of N-methylmorpholine in a 25 mL of carbon tetrachloride with dinitrogen tetroxide at dry ice temperature. The reaction is practically complete after 1 hr, but the system was kept overnight at the same temperature before it was treated any further. The excess oxides of nitrogen were removed, and the yellowish solid was filtered off, washed first with carbon tetrachloride and then with a little ethyl alcohol, dried and stored over P_4O_{10} in a vacuum desiccator. The yield (6.1 g), based on N-methylmorpholine, was 83%.

Anal. Calcd. for



C, 36.81; H, 6.80; N, 17.17. Found: C, 36.91; H, 7.08; N, 16.97.

The infrared data for the product are given in Table 1.3. The spectrum shows, among other bands, a very strong broad band in the region of 1440-1320 cm^{-1}. This region includes the most characteristic absorption due to the N O linkage and its stretching vibration which appears as an absorption of strong intensity at about 1300 cm^{-1}.[1] This region includes also the symmetrical stretching frequency for compounds containing the NO_2 group which absorbs in the region around 1380 cm^{-1}. The spectrum shows also a strong band at 865 cm^{-1} which is associated with

compounds containing NO_3^- group, which absorps strongly in the region of 860-800 cm^{-1}.

The ^1H NMR spectrum of the product is shown in Figure 1.10. The spectrum consists of five peaks: a sharp singlet and four broad peaks centered at 3.148, 3.549, 3.921 and 4.047 ppm. The ratios of relative areas are 3:2:2:2:2, respectively. The first peak is assigned to the three protons of the methyl group; the second and third peaks are assigned to the four protons of the two carbons adjacent to the nitrogen atom in the ring, namely carbon 3 and 5; the fourth and fifth peaks are assigned to the protons at the two carbons adjacent to the oxygen atom of the ring (C-2, C-6). The ^1H NMR data for N-methylmorpholine are given in Table 1.4 for comparison.

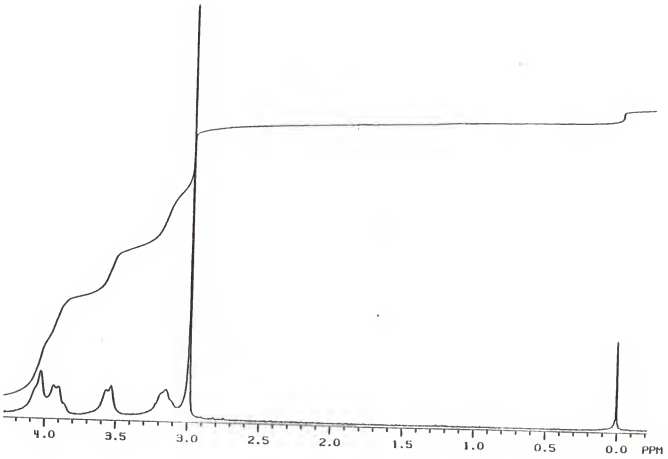
The ^{13}C NMR spectrum, Figure 1.11 (a,b), shows three different kinds of carbon atoms. The peak at 44.023 is a quartet and is assigned to the methyl carbon with a coupling constant J_{CH} of 143.03 Hz. The peak at 53.737 is a triplet and is assigned to the two carbon atoms next to the ring nitrogen, J_{CH} = 144.37 Hz. The peak at 63.430 is another triplet and is assigned to the two carbons adjacent to the ring oxygen with a carbon to hydrogen coupling of 146.77 Hz.

Reactions of N,N'-dimethylpiperazine with Dinitrogen Tetroxide

A solution of 0.028 mol of N,N'-dimethylpiperazine (bp 131-132°C) in 50 mL of carbon tetrachloride was allowed to react with dinitrogen tetroxide at dry ice temperature for 3 hr. Then the temperature was allowed to rise, and the system was kept at 0°C for 25 hr. The excess nitrogen oxides were removed, and the pale yellow solid was filtered off, washed five times with 10 mL portions of carbon tetrachloride, then the same with diethyl ether, and finally with 30 mL of hot ethanol.

Figure 1.10. The 300 MHz ^{1}H NMR spectrum of N-methylmorpholine N-oxide•N_2O_4 in DMSO-d6 solution.

H7629 , 000 CHEN 29.JUL84
NMM IN DMSO-D6
M. AL-SUBU



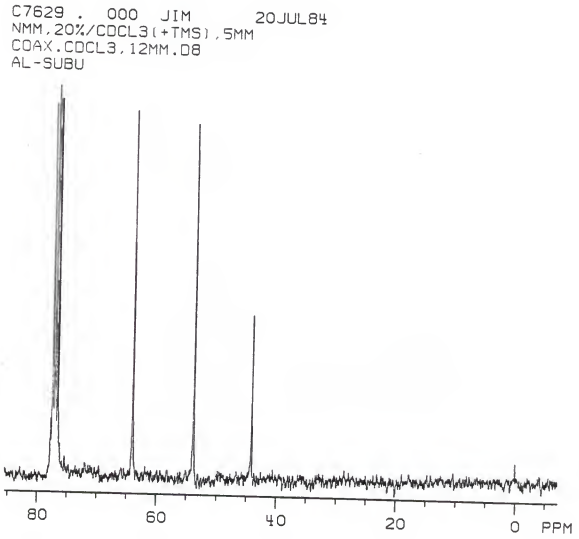
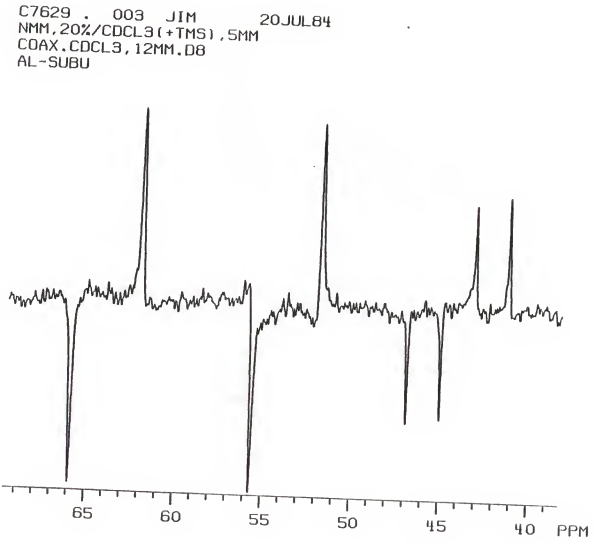


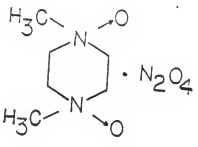
Figure 1.11. The 300 MHz ^{13}C NMR spectrum of N-methylmorpholine N-oxide• N_2O_4 in DMSO-d6 solution.

(a) Proton noise decoupled.

Figure 1.11 (continued). (b) The undecoupled ^{13}C NMR spectrum of N-methylmorpholine N-oxide•N_2O_4.


C7629 . 003 JIM 20JUL84
NMM,20%/CDCL3(+TMS),5MM
COAX.CDCL3,12MM.D8
AL-SUBU
65
60
55
50
45
40
PPM

The washed product was dried under reduced pressure. The resulting white solid (5.9 g), which was insoluble in a variety of organic solvents, darkened at 115°C, softened and shrunk at 175°C, and melted with decomposition at 218–220°C. The yield based on N,N-dimethylpiperazine was 88%.

Anal. Calcd. for 

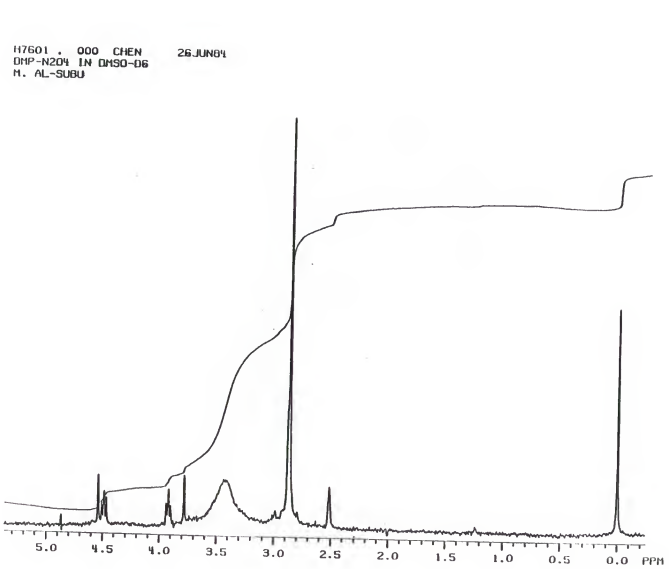
C, 30.25; H, 5.92; N, 23.52. Found: C,31.09; H, 6.68; N, 24.09.

Attempts to isolate the same product from the reaction of dinitrogen tetroxide with N,N'-dimethylpiperazine in the absence of a solvent always resulted in flame production.

The infrared data of the product are given in Table 1.3. The spectrum shows, together with other bands associated with N,N'-dimethylpiperazine, several strong bands in the region of 1470–1270 cm^{-1} as well as a strong absorption at 815 cm^{-1}. These absorptions, as mentioned earlier, include those characteristic bands for compounds containing $N^{+} \rightarrow O^{-}$, NO_2 and NO_3^{-} groups.

The ^1H NMR spectrum of the crude product is given in Figure 1.12. It shows two types of protons for the compound. The sharp singlet at 2.865 ppm is assigned to the protons of the two methyl groups. The broad peak centered at 3.423 ppm is assigned to the methylene protons. The relative area ratio of the two peaks above is approximately 3:4. The ^1H NMR data for N,N'-dimethylpiperazine are given in Table 1.4 for comparison.

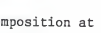
Figure 1.12. The 300 MHz ^{1}H NMR spectrum of N,N'-dimethyl-piperazine N,N'-dioxide•N_2O_4 in DMSO-d6 solution.


H7601 . 000 CHEN 26JUN84
DMP-N204 IN DMSO-D6
M. AL-SUBU
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
PPM

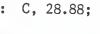
The ^{13}C NMR spectrum, Figure 1.13, shows two peaks: the first peak is at 42.951 and is assigned to the methyl carbons, the second one is at 50.341 ppm and is assigned to the methylene carbons.

Reactions of Triethylenediamine with Dinitrogen Tetroxide

(1). A mixture of about 3.1×10^{-3} mol of the extremely hygroscopic 1,4-diazabicyclo[2.2.2]octane, better known as triethylenediamine (mp 158-160°C), and a large excess of dinitrogen tetroxide was allowed to react at 0°C for 12 hr. After completion of the reaction, the remaining nitrogen oxides were removed. The white solid was stored in a desiccator under reduced pressure. The product started to shrink at 93-103°C and melted with decomposition at 178°C.

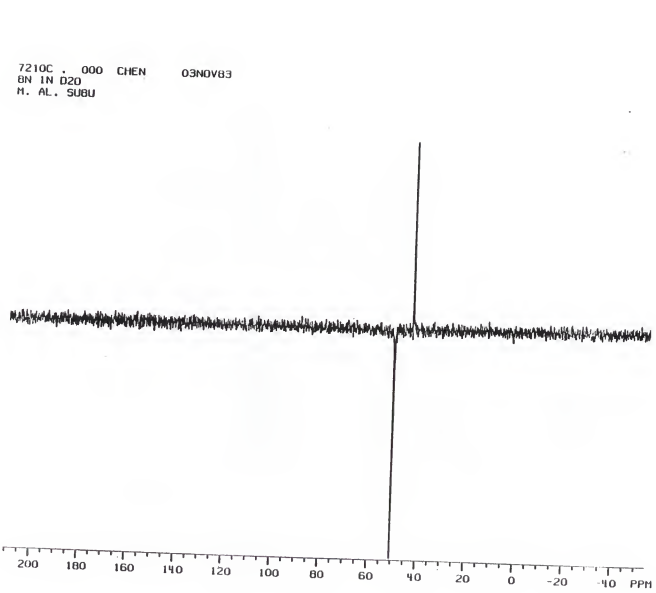
Anal. Calcd. for  : C, 28.35; H, 5.55; N, 22.04; O, 44.05. Found: C, 28.88; H, 5.51; N, 21.74; O, 43.87.

(2). The same product was obtained by the reaction of excess dinitrogen tetroxide with a solution of 0.02 mol of triethylenediamine in 40 mL of a diethyl ether-chloroform mixture (1:1 v/v) at dry ice-acetone temperature for 2 hr. The reaction mixture was kept overnight at 0°C before the excess nitrogen oxides were removed. The white crystals produced were filtered, washed twice with 25 mL of diethyl ether, dried, and stored in a vacuum desiccator. The amount of product obtained (4.8 g) corresponds to 94% yield based on the triethylenediamine used.

Anal. Calcd. for  : C, 28.35; H, 5.55; N, 22.04. Found: C, 28.25; H, 5.92; N, 22.97.

The infrared data for the product are given in Table 1.3. The spectrum shows a very strong, broad band in the region of 1450-250 cm^{-1},

Figure 1.13. Proton noise decoupled 300 MHz ^{13}C NMR spectrum of N,N'-dimethylpiperazine N,N'-dioxide•N_2O_4 adduct in D_2O solution.


7210C . 000 CHEN 03NOV83
BN IN D2O
M. AL. SUBU
200
180
160
140
120
100
80
60
40
20
0
-20
-40
PPM

which includes the absorptions assigned for compounds containing $N^+ \rightarrow O^-$ and NO_2 linkages. The spectrum shows also a strong absorption at 840 cm^{-1} which is in the absorption range assigned for ionic nitrates.

The ^1H NMR spectrum of the compound is shown in Figure 1.14. The spectrum consists of two peaks: a sharp singlet at 3.665 ppm assigned to the methylene protons and a broad peak centered at 10.16 ppm assigned to the -OH protons of the water molecule. The relative area ratio under the two peaks is about 6:1, respectively. The ^1H NMR data for triethylene diamine are given in Table 1.4 for comparison.

The ^{13}C NMR spectrum of the compound is given in Figure 1.15. The spectrum shows only one peak, viz, a sharp singlet at 43.169 ppm from TMS.

Reactions of 12-Crown-4 Ether with Dinitrogen Tetroxide

Excess dinitrogen tetroxide was added to 1.7621 g (0.01 mol) of 1,4,7,10-tetraoxacyclododecane [12-crown-4 (bp 160°C)]. The reaction was allowed to proceed for 20 min at -78°C, then warmed to 0°C, and kept at that temperature for 48 hr. The product, a white solid, was allowed to warm to room temperature, at which time the excess dinitrogen tetroxide was removed and the reaction mixture, now a brown viscous oil, was reweighed (2.234 g). Mole ratio N_2O_4:12-crown-4 ether ≃2:1.

Anal. Calcd. for 12-crown-4·N_2O_4·H_2O: C, 37.21; H, 7.80; N, 5.43; O, 49.56. Found: C, 37.38; H, 6.61; N, 5.89; O, 50.06.

Several attempts to isolate a solid product, stable above 0°C, from the reaction mixture of 12-crown-4 ether with dinitrogen tetroxide in chloroform or diethyl ether were unsuccessful.

Figure 1.14. The 300 MHz ^{1}H NMR spectrum of triethylenediamine N,N'-dioxide•N_2O_4 in DMSO-d6 solution.

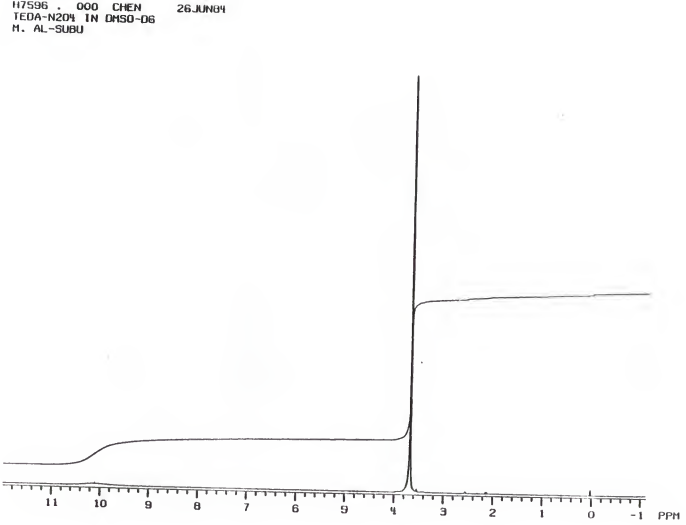
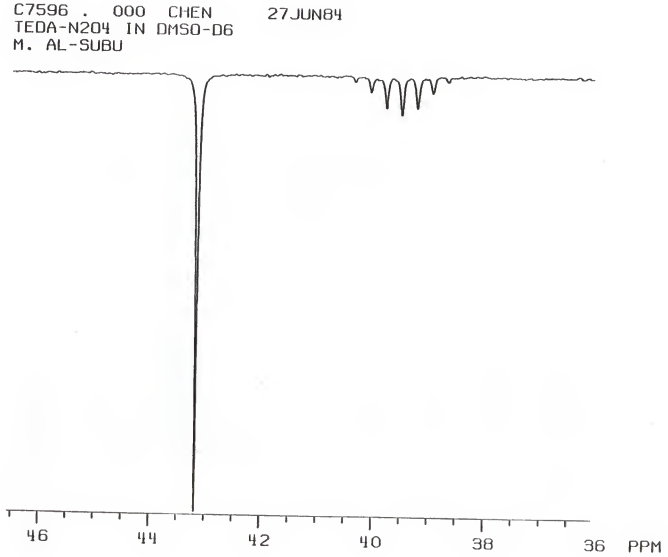

H7596 . 000 CHEN 26JUN84
TEDA-N2O4 IN DMSO-D6
M. AL-SUBU
11
10
9
8
7
6
5
4
3
2
1
0
-1
PPM

Figure 1.15. Proton noise decoupled 300 MHz ^{13}C NMR spectrum of triethylenediamine N,N'-dioxide$\cdot N_2O_4$ in DMSO-d6 solution.


C7596 . 000 CHEN 27JUN84
TEDA-N204 IN DMSO-D6
M. AL-SUBU
46
44
42
40
38
36
PPM

Reactions of 15-Crown-5 Ether with Dinitrogen Tetroxide

(1). Excess dinitrogen tetroxide and 2.2027 g (0.01 mol) of 1,4,7,10,13-pentaoxacyclopentadecane [known as 15-crown-5 ether; bp 100-135°C (0.2 mm)] were allowed to react at 0°C for 12 hr. The unreacted dinitrogen tetroxide was then removed. The weight of the resulting white solid was 2.6585 g (mp 10°C). Mole ratio: N_2O_4 crown ether = 0.5.

Anal. Calcd. for (15-crown-5)$_2$·N_2O_4: C, 45.11; H, 7.57; N, 5.26. Found: C, 46.26; H, 7.37; N, 5.05.

(2). In 35 mL diethyl ether, 2.5 g (1.13×10^{-2} mol) of 15-crown-5 ether was treated with dinitrogen tetroxide at dry ice temperature for a few minutes. It was noticed that the whole reaction mixture solidified to a light blue solid that, upon warming to 0°C, partially melted to give a white solid in a brownish solution. The solid was filtered, washed with ether, and dried (mp 8-10°C). The weight of the product was 2.1 g.

Anal. Calcd. for (15-crown-5)$_2$·N_2O_4·$4H_2O$: C, 39.72; H, 8.01; N, 4.63. Found: C, 39.18; H, 7.79; N, 4.02.

Reactions of 18-Crown-6 Ether with Dinitrogen Tetroxide

(1). A mixture of 1.4478 g (5.5×10^{-3} mol) of 1,4,7,10,13,16-hexaoxacyclooctadecane, better known as 18-crown-6 ether (mp 39-40°C), and a large excess of dinitrogen tetroxide was allowed to react at 0°C for 5 days. After the removal of unreacted dinitrogen tetroxide, the weight of the white solid product was 1.9940 g (started to give off brown gas at 82°C and melted at 91-92°C). Mole ratio N_2O_4:crown ether = 1.08.

Anal. Calcd. for 18-crown-6·N_2O_4: C, 40.44; H, 6.78; N, 7.86. Found: C, 36.10; H, 6.16; N, 8.27.

(2). About 2.78 g (0.01 mol) of 18-crown-6 ether in 50 mL of diethyl ether was allowed to react with dinitrogen tetroxide at dry ice

temperature for about 1 hr. The reaction mixture appeared to be a homogeneous green-yellow solid. It was warmed to 0°C and kept at that temperature for 12 hr. The white solid obtained was collected by filtration, washed with diethyl ether, and dried. The solid (2.92 g) started to lose N_2O_4 at 80°C and melted with decomposition at 92°C.

Anal. Calcd. for 18-crown-6·N_2O_4·$2H_2O$: C, 36.73; H, 7.19; N, 7.14. Found: C, 36.34; H, 6.73; N, 6.96.

It is clear that the adduct loses dinitrogen tetroxide; drying the above compound under reduced pressure for 1 hr gave C, 50.90; H, 8.20; N, 0.44. Calcd. for 18-crown-6 ether: C, 53.52; H, 10.8%.

Reactions of Dicyclohexyl-18-Crown-6 Ether with Dinitrogen Tetroxide

About 2.3 g (6.2×10^{-3} mol) of 2,3,11,12-dicyclohexyl-1,4,7,10,13,16-hexaoxacyclooctadecane (common name, dicyclohexyl-18-crown-6 ether; mp 36-56°C), in 20mL diethyl ether was treated with dinitrogen tetroxide at dry ice temperature. On being warmed, the color of the reaction mixture changed from deep blue to a white solid in a greenish solution at 0°C. The white crystals were filtered, washed with diethyl ether, and dried. The crystals lost some N_2O_4 and changed to an oily material on warming to room temperature.

Anal. Calcd. for dicyclohexyl-18-crown-6·N_2O_4·$4H_2O$: C, 44.77; H, 8.26; N, 5.22; O, 41.75. Found: C, 44.60; H, 8.08; N, 5.59; O, 41.73.

Drying the above adduct under reduced pressure for 1 hr gave the following analysis: C, 61.37; H, 9.69; N, 0.98.

Reactions of Dicyclohexyl-24-Crown-8 Ether with Dinitrogen Tetroxide

About 10 g (2.2×10^{-3} mol) of 2,3,14,15-dicyclohexyl-1,4,7,10,13,16,19,22-octaoxacyclotetracosane (known as dicyclohexyl-24-crown-8 ether) was allowed to react with dinitrogen tetroxide at 0°C for

12 hr. Excess dinitrogen tetroxide was removed over a period of 10 hr, at which time the product was a brown viscous oil which did not solidify at temperatures as low as -78°C.

Attempts to isolate solid products from the reaction of the crown ether with dinitrogen tetroxide in diethyl ether, pet.ether, or chloroform were unsuccessful.

Anal. Calcd. for dicyclohexyl-24-crown-8 $\cdot N_2O_4 \cdot 2H_2O$: C, 48.96; H, 8.22; N, 4.76; O, 38.05. Found: C, 47.48; H, 7.98; N, 4.89; O, 38.47.

The infrared data for the products obtained from the reactions of dinitrogen tetroxide with the 18-crown-6 ether, dicyclohexyl-18-crown-6 ether, and dicyclohexyl-24-crown-8 ether are given in Table 1.3. Each of the products shows, besides those bands of the crown ether, three absorptions at about 1800, 1375 and 820 cm^{-1}. The first band, at ~1800, is associated with compounds containing the nitrosonium ion NO^+; the second and third are associated with compounds containing the nitrate ion NO_3^-.

The Raman spectrum of the product from the reaction of dinitrogen tetroxide with 18-crown-6 ether was obtained on a crystalline solid using a spex Raman instrument and the green line of an argon laser. The data are given in Table 1.5. The spectrum shows two frequencies that are present in the spectrum of the product but are completely absent from the spectrum of dinitrogen tetroxide and the spectrum of the crown ether. The two frequencies are 2265 and 1035 cm^{-3} which can be nothing else than the nitrosonium ion and the nitrate ion fundamentals.[34]

Electron paramagnetic resonance (epr) measurements were done on solid samples of the 18-crown-6$\cdot N_2O_4$ product using an IBM ER-200D spectrometer. A spectrometer frequency of 9.41 GHz and a modulation frequency of 100 KHz were used. The spectrum that was recorded at room temperature showed no bands at all.

Table 1.5

Raman Absorption in (cm^{-1})[a] for 18-Crown-6•N_2O_4[b]

3150 (w)	2910 (b,s),	2855 (b,m)
2265 (vs) ,	1475 (m) ,	1320 (m)
1270 (m) ,	1250 (w) ,	1035 (b,w)

a Frequencies are accurate to ±3 cm^{-1}.

b b, Broad; m, medium; s, strong; v, very; w, weak.

Reactions of Dibenzo-18-Crown-6 Ether with Dinitrogen Tetroxide

(1). A mixture of dinitrogen tetroxide and 1.2280 g (3.4×10^{-3} mol) dibenzo-18-crown-6 ether (or 2,3,11,12-dibenzo-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-diene; mp 162-164°C) was allowed to react at dry ice-acetone temperature. As the temperature was allowed to rise, reaction began even before the temperature reached 0°C, as indicated by the formation of a yellow solid together with a little black solid. The reaction was kept for 15 hr at 0°C before excess nitrogen oxides were removed. The yellow solid was washed with diethyl ether and dried; it weighed 1.5591 g. The mole ratio of N_2O_4 to crown ether was 1.06; the mp was 195-200°C.

Anal. Calcd. for dinitro-dibenzo-18-crown-6 ether: C, 53.11; H, 5.34; N, 6.19. Found: C, 50.64; H, 5.25; N, 6.25.

(2). About 2.1 g (5.8×10^{-3} mol) of dibenzo-18-crown-6 ether was dissolved in 50 mL of chlorobenzene. As soon as dinitrogen tetroxide was distilled into the solution at dry ice temperature, a vigorous reaction began giving a yellowish solid together with some black deposit on the walls and surface of the reaction flask. The solid was filtered, washed first with chlorobenzene, then with ethanol, and finally three times with 40 mL portions of diethyl ether. The dried solid weighed 2.3 g (mp 200-205°C).

Anal. Calcd. for dinitro-dibenzo-18-crown-6 ether: C, 53.11; H, 5.34; N, 6.19. Found: C, 53.20; H, 5.27; N, 6.11.

The crude product was recrystallized from hot 2-methoxyethanol. The ultraviolet spectrum, Figure 1.16, of the recrystallized product as recorded on a Pye Unicam ultraviolet-visible spectrophotometer Model 8800 at room temperature using spectral grade chloroform as the solvent in 1 cm square quartz cell.

Figure 1.16. Ultraviolet spectrum of dinitrodibenzo-18-crown ether in $CHCl_3$ solution.

PU 8600
PYE UNICAM
WAVELENGTH nm
START λ : 600.0
MAI RT : 600.0
STOP λ : 220.0
MONOCHROMATOR
SPEED : 2 nm/s
BANDWIDTH : 2 nm
CYCLE
: 001 : 000
TIME 100.00:100.00
MESSAGE
SPHW : 1.0 A
OFFSET : 0.000 A
SCALE : 10 nm/cm
RESPONSE : 2 s
CELL : 1
DATE 08.06.84
OPERATOR 000
HS 450-300 SC 0-1
CELL : λ nm : A
1 : 297.3 : 0.029
2 : 277.7 : 0.025
A 1.000
0.800
0.600
0.400
0.200
0.000
600.0
200.0
401.0
λ SCALE : 20.00 nm

$\lambda_{max}^{CHCl_3}$ (nm)	Log ε_{max}
337.3	4.1585
277.7	4.9685

The infrared data are given in Table 1.3. The spectrum shows strong bands at 1510 and 1340 cm^{-1} which are associated with aromatic nitro compounds. It shows also the characteristic overtone and combination band pattern for 1,2,4-trisubstituted benzene derivative at 1740-1680 cm^{-1}.

The ^1H NMR spectrum is given in Figure 1.17 (a,b). The spectrum confirms the 1,2,4,-trisubstituted structure for the product; H_a couples with H_c but not H_d. It shows H_c as a quartet centered at 7.897 ppm (J_{meta} = 2.51, J_{ortho} = 8.94 Hz), H_a a doublet centered at 7.27 ppm and H_d a doublet centered at 7.166 ppm. Interestingly, the spectrum does not show the aliphatic protons of the product as one singlet as in the case of dibenzo-18-crown-6 ether, but instead it shows two singlets, one at 4.219 ppm and the other at 3.859 ppm. These are attributed to the protons on carbon 5, 9, 14, 18 and carbons 6, 8, 15, 17, respectively.

The ^{13}C NMR spectrum, Figure 1.18, consists of seven peaks located at 153.732, 147.641, 140.541, 117.606, 111.242, 106.544 and 68.395 ppm and are attributed to the carbon atoms (3,11), (2,12), (b), (c), (d), (a), and the aliphatic carbon atoms, respectively.

Discussion and Conclusions

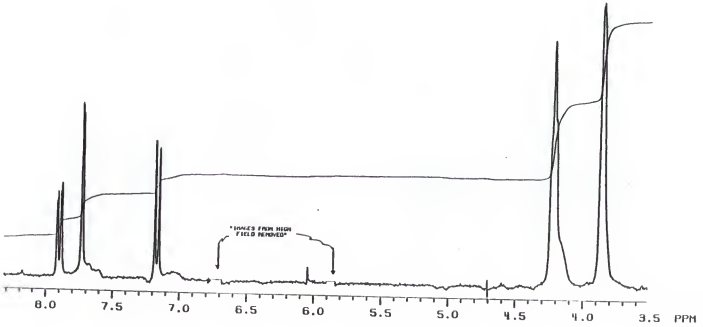
The Reaction with 1,4-Thioxane

Numerous methods are known for the transformation of organic sulfides to sulfoxides utilizing such reagents as nitric acid or hydrogen

Figure 1.17. The 300 MHz ^{1}H NMR spectrum of dinitrodibenzo-18-crown-6 ether in saturated DMSO-d6 solution at 21°C.

(a) Aliphatic and aromatic protons.

H7570 . 000 JIM 15JUN04
"NDBC" SAT'D SOLN/DMSO-D6
SMM. AL-SUBU.



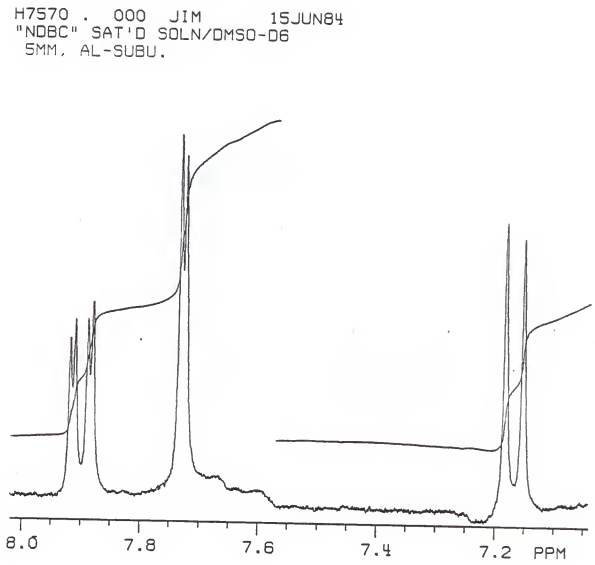
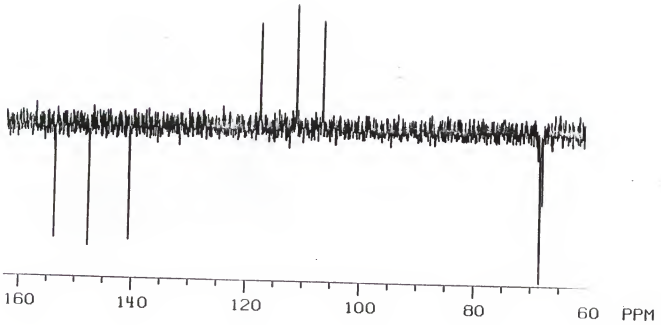


Figure 1.17 (continued). (b) The ^{1}H NMR spectrum of the aromatic region of dinitrodibenzo-18-crown-6 ether, with expansion.

Figure 1.18. Proton noise decoupled 300 MHz ^{13}C NMR spectrum of dinitrodibenzo-18-crown-6 ether in DMSO-d6 solution at 21°C.

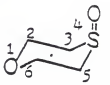
C7570 . 000 ROCCA 12JUN84
NDBC IN DMSO-D6 (SAT'D)
SMM. M. AL-SUBU



peroxide.[35] For example, 1,4-thioxane 4-oxide is obtained from the oxidation of 1,4-thioxane by sodium metaperiodate.[33] Our results show that 1,4-thioxane 4-oxide can be obtained in high yields from the reaction of liquid dinitrogen tetroxide with pure 1,4-thioxane or its solution in carbon tetrachloride.

The infrared spectral data of the product are summarized in Table 1.3. The absorption of the S=O bond at ~1550 cm^{-1} is in agreement with the values reported in the literature.[33]

The ^1H NMR spectrum for our product is shown in Figure 1.8 (a), and the spectral data are in Table 1.4. This spectrum is consistent with the reported spectra[36,37] and has been resolved [Figure 1.8 (b)] in more detail; additional coupling constants have been calculated and more peaks are assigned. This spectrum is also consistent with the assumption that the sulfur-oxygen bond favors the axial conformation as is indicated by the values of the coupling constants. The multiplet centered at 4.364 is assigned to the axial hydrogens at C-2 and C-6.



The multiplet centered at δ 3.828 is assigned to the equatorial hydrogen atoms at C-2 and C-6. The multiplet at δ 2.956 is assigned to the axial hydrogen atoms at C-5 and C-3; the one at higher field, namely, δ2.744, is assigned to the equatorial hydrogen atoms. The calculated coupling constants are $J_{2A,2E} = J_{6A,6E} = 12.8$ Hz (lit. 13), $J_{2A,3A} = J_{6A,5A} = 9.9$ Hz (lit 9 Hz), $J_{2A,3E} = J_{6A,5E} = 2.1$ Hz (not reported),

$J_{2E,3A} = J_{6E,5A} = 3.9$ Hz (lit 4.5 Hz), $J_{3A,3E} = J_{5A,5E} = 13.3$ Hz (not reported), $J_{3E,2E} = 4.3$ Hz (not reported), and they are consistent with the assignments above.

Compared with the ^1H NMR spectrum of 1,4-thioxane (Table 1.4), a downfield shift is noticed for the axial hydrogens at C-2 and C-6 which might be explained as resulting from the acetylene-like anisotropy of the axial S=O bond. The upfield shift of the equatorial hydrogen atoms at C-2 and C-6 might be explained by similar reasoning.

The ^{13}C NMR spectrum of our product, Figure 1.9 (a,b) and Table 1.4, is consistent with the reported spectra[35,36] and supports the conclusion concerning axial conformation of the S=O bond. The assignment of the chemical shifts is made by comparison with the reported spectra; however, the carbon-hydrogen coupling constants are reported for the first time. The obtained spectrum consists of two triplets; the one centered at δ 59.127 with a coupling constant J_{CH} of about 139 Hz is assigned to C-2 and C-5; the other at higher field namely, δ 46.309 with a coupling constant J_{CH} of about 147 Hz, is assigned to C-3 and C-5.

The 1,4-thioxane 4-oxide has several practical applications in industry. It is a powerful solvent and can be used in cosmetics, varnishes, etc. It is also used as a solvent for polyacrylonitrile to form solutions which are suitable for immediate conversion to shaped articles in which the discoloration during polymerization is reduced.[38] After this work was completed, it was found that the preparation of 1,4-thioxane 4-oxide from 1,4-thioxane and N_2O_4 has been reported.[39] However, no experimental data of any kind are given in this report.

Although 1,4-thioxane 4-oxide has a polar S=O bond and an ether oxygen, it does not form an adduct with dinitrogen tetroxide. This might

be explained by the fact that the S=O bond is made up of a σ S–O bond and two weak bonds at right angles to each other. The weak bonds are formed by the overlap of the p orbitals of the oxygen atom with the d orbitals of the sulfur atom. This reduces the p character of the oxygen lone pair which makes it less basic. The ether oxygen might be capable of forming an adduct, but only at low temperatures, like diethyl ether in which the oxygen atom is even more basic than in our product.

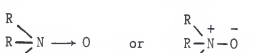
The Reactions with Nitrogen Bases

Our experimental data indicate that the tertiary amines used in this study, namely N-methylmorpholine, N,N'-dimethylpiperazine, and triethylenediamine, react with dinitrogen tetroxide to give the corresponding amine oxides. The N-methylamine N-oxide or the N,N'-dimethylamine N,N'-dioxide in each case reacts further with dinitrogen tetroxide to give adducts which are formulated as complexes of nitrosyl nitrate rather than as molecular adducts.

These results are consistent with the fact that some aliphatic tertiary amines react with oxidizing agents such as hydrogen peroxide to give the tertiary amine oxide.

$$R_3N: + \ddot{O}: \longrightarrow R_3N:\ddot{O}:$$

The structure of amine oxides can be represented as



where the linkage between the nitrogen and the oxygen atoms is a single bond.[40-43] The formation of the amine oxides in our work is also indicated by the physical properties of the products as compared with the

reactants and which, in agreement with the general description of amine oxides, are solids of relatively high melting points, low volatility, low solubility in organic solvents, but high solubility in water, with a tendency to form hydrates.

The further reactions of the amine oxides with dinitrogen tetroxide to form adducts is also expected as a result of the most common property of amine oxides which is the large dipole moment. For comparison, Table 1.6 shows the properties of trimethylamine and its N-oxide.

Table 1.6

Properties of Trimethylamine and Trimethylamine N-oxide

	bp (°C)	mp (°C)	μ (D)	pKa
Trimethylamine N-oxide	-	212	5.02	4.65
Trimethylamine	70	liquid	0.65	9.74

The infrared spectral data for the products are summarized in Table 1.3. The three products show very similar strong, broad absorptions in the region 1450-1250 cm^{-1} which suggest multiple bands rather than single ones. This region of the infrared spectrum contains the most characteristic absorption resulting from the $N^{+}-O^{-}$ linkage, and it also contains the symmetrical stretching frequency for compounds containing O-N-O group. These spectra also show strong absorptions in the region 800-860 cm^{-1} which is the range attributed to ionic nitrates.

The NMR spectra of the products (Figures 1.10, 1.12 and 1.14) are summarized in Table 1.4. The spectra were discussed earlier in this chapter and are as expected according to the number of protons and their relative positions in each compound. It is especially noteworthy that

there is a downfield shift of δ_H values for all hydrogen atoms in the compound upon quaternization of the nitrogen atom. This shift is about 0.8-1.0 ppm for the methylene protons next to the quaternary nitrogen, about 0.5-0.7 ppm for the methyl protons in the products of N-methylmorpholine, and N,N'-dimethylpiperazine and about 0.3 ppm for the methylene protons attached to the ether oxygen in the N-methylmorpholine product. This shift is to be expected, since quaternization results in a decrease in electron density on the nitrogen atom, which has an electron withdrawing effect on the alkyl group protons.

The ^{13}C NMR spectra (Figures 1.11, 1.13 and 1.15) were analyzed earlier in this chapter. The chemical shifts, available coupling constants, and the assignment of the peaks are summarized in Table 1.4. The number of peaks in each spectrum is consistent with the number of magnetically different carbon atoms in the corresponding compound: three peaks for the N-methylmorpholine N-oxide-N_2O_4 adduct, two peaks for the N,N'-dimethylpiperazine N,N'-dioxide-N_2O_4 adduct, and one peak for the ethylenediamine N,N'-dioxide-N_2O_4 adduct.

Previous studies on the resolution of optical isomers of amine oxides having three different R groups show that these groups and the O atom take up a tetrahedral position in relation to the nitrogen atom.[39] It was also mentioned in the introduction of this chapter that in the equilibrium

$$\underset{\text{ionic}}{[(B)_nNO][NO_3]} \rightleftharpoons nB + N_2O_4 \rightleftharpoons \underset{\text{molecular}}{N_2O_4 \cdot nB}$$

strong electron donors shift the equilibrium to the left to give ionic complexes. The results obtained in this work support the above formulation with n=2 for N-methylmorpholine N-oxide since it has only one N→O

bond, and n=1 for those having two N→O bonds per molecule, namely N,N'-dimethylpiperazine N,N'-dioxide and triethylenediamine N,N'-dioxide. The structures of the first two compounds might be represented as shown in Figure 1.19 (a,b). The structure of the third compound is assumed to be similar to Figure 1.19 (b).

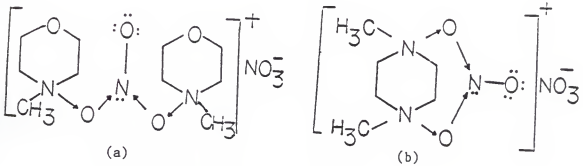


Figure 1.19. Probable structures of (a) N-methylmorpholine N-oxide-N_2O_4 adduct and (b) N,N'-dimethylpiperazine N,N'-dioxide N_2O_4 adduct.

Reactions with Crown Ethers

The reaction of dinitrogen tetroxide with the crown ethers used in this study shows that these reactions are of two types: (1) Aliphatic crown ethers form adducts with N_2O_4 in which the mole ratio of the crown ether to N_2O_4 is either 1 or 2 depending on the size of the cavity of the crown ether; 18-crown-6 ether, dicyclohexyl-18-crown-6 ether, and dicyclohexyl-24-crown-6 ethers form 1:1 adducts whereas 15-crown-5 and 12-crown-4 ethers form 2:1 adducts. (2) The aromatic crown ether, namely dibenzo-18-crown-6 ether undergo nitration at the aromatic ring rather than forming an adduct.

The infrared spectra of some of the products are summarized in Table 1.3. The spectra of the componds show common absorptions at

~1800, ~1375 and ~820 cm^{-1}. The absorption at ~1800 cm^{-1} was assigned to the NO^+ ion in compounds like NO^+Br^- and NO^+Cl^-. The absorptions at ~1375 and ~820 cm^{-1} are associated with compounds containing the nitrate ion NO_3^-.

Because the 18-crown-6 ether·N_2O_4 adduct is the most stable among the crown ether adducts isolated in this study, other measurements such as Raman and electron paramagnetic resonance were carried out on this adduct for further identification.

The Raman spectral data of the adduct are summarized in Table 1.5. The spectrum shows two absorptions present in the product but completely absent from the spectra of the reactants. These two absorptions (at ~2265 and 1035 cm^{-1}) are the fundamentals of the nitrosonium ion and the nitrate ion, respectively.[34]

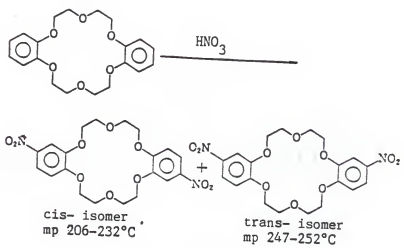
The electron paramagnetic resonance spectra (epr) of solid samples show no bands at all, thus indicating that the adducts do not contain "odd" molecules such as NO_2.

It is clear from the experimental results that the adducts of the aliphatic crown ethers with N_2O_4 are better formulated as nitrosyl nitrate than as molecular adducts of N_2O_4 as is indicated by their IR and Raman spectra.

The force that holds the crown ether and the nitrosyl ion together in the adduct is believed to be ion-dipole interaction between the positive end of the nitrosyl ion (nitrogen) and the coplanar negatively charged oxygen atoms on the polyether ring. This assumption is made according to the general manner of complexation of crown ethers with other ions. More studies need to be done, probably x-ray, to determine the exact nature of these adducts.

The reaction of dibenzo-18-crown-6 ether with dinitrogen tetroxide is different from the rest of crown ethers examined in this study. The experimental data show that dibenzo-18-crown-6 ether reacts with dinitrogen tetroxide to yield a nitrated product rather than an adduct. The substitution on the aromatic rings of the ether is believed to follow the general rules of orientation in electrophilic aromatic substitution, namely, the -OR group is an activating ortho para director.

Feigenbaum and Michel[44] prepared an isomeric mixture (cis and trans) of 4,4'-dinitrodibenzo-18-crown-6 ether by the nitration of dibenzo-18-crown-6 ether using a mixture of nitric acid and acetic acid in chloroform-acetic acid solution.



The suggested structures of the two isomers are not certain; however, the one with the higher melting point and lower solubility in a variety of solvents was assigned the trans structure on symmetry bases.

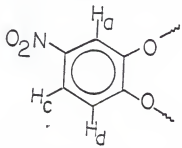
The product isolated in the present work is completely soluble in hot 2-methoxyethanol and melts over a rather small range (200-205°C)

which, according to Shchori et al.,[45] should be assigned the cis structure.

The ultra-violet spectrum of the product measured in chloroform is shown in Figure 1.6. The spectrum shows two maxima, namely λ_{max} 337.3 and λ_{max} 277.7 nm with log ϵ_{max} = 4.1585 and 4.9685, respectively.

The infrared spectral data are summarized in Table 1.3. The two strong absorptions at 1510 and 1340 cm^{-1} are associated with aromatic nitro compounds. The characteristic overtone and combination band pattern expected for 1,2,4-trisubstituted benzene derivatives is shown in the region 1740-1680 cm^{-1}.

The ^1H NMR spectrum (Figure 1.7) also confirms the 1,2,4-trisubstituted structure for the product; H_a couples with H_c but not H_d. The



H_c is shown as a quartet centered at δ 7.897 with coupling constants J_{meta} ~ 2.5 Hz and J_{ortho} ~ 9 Hz. The two doublets centered at δ 7.27 and δ 7.166 are assigned to H_a and H_d, respectively. The spectrum is consistent with the reported part of the ^1H NMR spectrum of the cis isomer and gives even more evidence for the 1,2,4-trisubstituted structure of the benzene rings in the compound as it is indicated by the values of the proton-proton coupling constants J_{ortho} and J_{meta}. One notable feature in the spectrum is that the aliphatic protons of the dinitro derivative are shown as two singlets: δ 4.219 and δ 3.859 compared with only one peak δ 3.80-4.30 in the parent crown ether.

The ^{13}C NMR spectrum of the product is given in Figure 1.18. The ^{13}C chemical shift assignments are made by comparison with the calculated values based on substituent effects on the ^{13}C shift in benzenes. The spectrum consists of seven peaks located at δ 153.732, 147.641, 140.541, 117.606, 111.242, 106.544 and 68.395 and are assigned as shown in Table 1.4.

Dinitrodibenzo-18-crown-6 ether is an important compound because upon reduction it gives the diaminedibenzo-18-crown-6 ether. The latter is polymerized with reagents such as terophtaloyl chloride, and the resulting polymers have several applications such as the capture of cations from aqueous solutions,[46] reverse osmosis membranes,[47] as well as many other applications.

The results show that neither dibenzo-18-crown-6 ether nor its dinitro derivative forms adducts with dinitrogen tetroxide. This might be explained as follows: Dibenzo-18-crown-6 ether is an 18-crown-6 ether in which two CH_2-CH_2 units in 18-crown-6 are replaced by two benzo units. This reduces the electron density at the oxygen atoms in the ring which results in a marked drop in the binding tendencies of the crown ether. Similar results are reported in the literature.[48] In the case of the dinitro derivative, the strongly electrophilic nitro group reduces the electron density at the oxygen atoms more than in the unsubstituted dibenzo-18-crown-6 ether which makes the formation of adducts even less likely.

Summary

The reactions of N_2O_4 with some crown ethers and other alicyclic nitrogen, oxygen and sulfur bases have been studied and the products from

each reaction identified based on the experimental data and by comparison with other reported reactions.

The reaction of N_2O_4 with 1,4-thioxane results in the oxidation of the sulfur atom to yield 1,4-thioxane 4-oxide, a compound which has several applications in industry. The disability of this compound to further react with N_2O_4 to form adducts is explained as a result of the low basicity of the oxygen atom in S=O bond, and the unstability of the adduct that would result in case that the ether oxygen atom is involved.

It is also concluded that the reactions of N_2O_4 with the tertiary amines; N-methylmorpholine, N,N'-dimethylpiperazine, and triethylenediamine result in the oxidation of the amine to the amine N-oxide or the amine N,N'-dioxide. However, the large dipole moment of the N^+-O^- bond causes the resulting amine oxides to react further with N_2O_4 to give adducts in which the ratio of the amine oxide to N_2O_4 is 2:1 or 1:1 depending on the number of the N^+-O^- bonds per molecule of the amine oxide. These adducts are believed to be complexes of nitrosyl nitrate rather than molecular adducts.

The reactions of N_2O_4 with the crown ethers result in two different types of products depending on whether the crown ether is aliphatic or contains aromatic groups. Aliphatic crown ethers form adducts with N_2O_4 in which the ratio of the crown ether to N_2O_4 is 1:1 for the ethers with the large cavity size (6 or 8 oxygen atoms) and 2:1 for those with smaller cavities (4 or 5 oxygen atoms). The adducts are also believed to contain ionic nitrosyl nitrate rather than molecular N_2O_4. The reactions of N_2O_4 with dibenzo-18-crown-6 ether result in the itration of the two benzo units to give the dinitro derivative and only in one isomeric form which, according to data published in the literature, is believed to be the cis-isomer.

The different behavior of dibenzo-18-crown-6 ether from the rest of crown ethers studied in this chapter is believed to result from the low electron density on the oxygen atoms of dibenzo-18-crown-6 ether because of the electron withdrawing effect of the aromatic rings.

CHAPTER TWO

A STUDY OF CHLORAMINATION OF DI- AND TRI-ALLYLAMINES

Introduction

The chloramine molecule has been shown to react with electron-donor molecules in accordance with the equation

$$B: + NH_2Cl \longrightarrow B:NH_2^+Cl^-$$

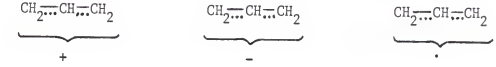
Among the Lewis bases where chloraminations have been studied are those containing one or more nitrogen, phosphorus, arsenic, antimony, sulfur, or selenium atoms as basic centers. Chloramine also reacts with ordinary olefinic double bonds under U-V irradiation or at high temperatures, but it adds on to the carbon-carbon double bond of ketenes even in the dark.

The reaction of chloramine with 1,1-disubstituted hydrazines R_2NNH_2 has received considerable attention as a source of 2,2-disubstituted triazanium chlorides, $[R_2N(NH_2)_2]Cl$. These salts are of interest because they contain the -N-N-N- chain and yet are stable at ordinary temperatures. Several triazanium salts were prepared by this method with R representing an alkyl or phenyl group.

The objective of this study was to extend the chloramination reaction to produce 2,2-disubstituted triazanium chloride in which R is in an unsaturated aliphatic group. However, the electrophilic chloramine might polarize the π-electron cloud in the unsaturated group and add to the

double bond in a manner analogous to the addition of other electrophilic reagents, such as halogens or hydrogen halides.

Lewis bases in which the allyl group is part of the molecule are of special interest because they undergo several types of reactions resulting from the stability of allyl cation, anion, or free radical.



Therefore, the chloramination of di- and tri-allylamine to form diallyltriazanium chloride and triallylhydrazinium chloride, respectively, was investigated; further, the polymerization of diallyltriazanium chloride to produce a high-energy polymer possibly suitable for incorporation in a solid rocket fuel was investigated.

Historical Background

Preparation in Aqueous Solution

The preparation of dilute aqueous solutions of chloramine by reaction of aqueous ammonia with sodium hypochlorite solutions at 0°C was reported by Raschig in 1907.[49]

$$NH_3 + OCl^- \rightarrow NH_2Cl + OH^-$$

The above reaction yields at best only about 0.25 M aqueous chloramine solutions at NH_3:OCl^- mole ratios of three to one.

Preparation in Gas Phase

It was not until 1951 that formation of chloramine by a gas phase reaction was reported by Sisler et al.,[50-52] allowing the convenient

preparation of anhydrous solutions of chloramine. This process was based on the reaction of gaseous chlorine with gaseous ammonia.

$$Cl_{2(g)} + 2NH_{3(g)} \longrightarrow NH_2Cl_{(g)} + NH_4Cl_{(s)}$$

Yields of 90% are obtainable at NH_3:Cl_2 mole ratios of 2.1/1.[53]

Chemical Reactions

Chloramine is an extremely versatile molecule in its chemical reactions. Its best-known reactions are those in which it aminates electron-donor species, presumably by bimolecular nucleophilic displacement (S_N2).[54-56]

The various reactions of chloramine with amines and hydrazines have been investigated extensively.[57-68] Chloramine reacts with liquid ammonia[58] to give the well-known rocket fuel hydrazine:

$$2NH_3 + NH_2Cl \longrightarrow NH_2NH_2 + NH_4Cl$$

Alkylamines react with a chloramine-ammonia mixture to produce alkylhydrazines.[67]

$$2RNH_2 + NH_2Cl \longrightarrow RNH\text{-}NH_2 + [RNH_3]Cl$$

If the Lewis base is a secondary amine such as dimethylamine, a disubstituted hydrazine is obtained;[62,67]

$$2(CH_3)_2NH + NH_2Cl \longrightarrow (CH_3)_2NNH_2 + [(CH_3)_2NH_2]Cl$$

1,1-dimethylhydrazine is a major component of a rocket fuel used in the space program and in the Titan III ballistic missile. Chloramination of trialkylamines has been reported to produce very high yields of 1,1,1-trisubstituted hydrazinium chlorides.[57,64]

$$R_3N + NH_2Cl \longrightarrow [R_3NNH_2]Cl$$

The reactions of substituted hydrazines with chloramine have been investigated undervarious conditions.[59,60,62-68] With 1,1-disubstituted hydrazines, the corresponding 2,2-disubstituted triazanium chlorides are obtained as stablecrystalline solids.

$$R_2NNH_2 + NH_2Cl \longrightarrow [R_2N(NH_2)_2]Cl$$

Extensive discussions of the reactions of chloramine with phosphorus nucleophiles have appeared.[54,57,69-85] Phosphine and primary and secondary phosphines react with chloramine to give a polymric phosphorus hydride (P_xH_y), tetrasubstituted phosphetane [$(RP)_4$], and tetrasubstituted biphosphine (R_2P-PR_2), respectively.[74] The reactions of chloramine with tertiary phosphines produce aminophosphonium chloride.[75]

$$R_3P: + NH_2Cl \longrightarrow [R_3PNH_2]Cl$$

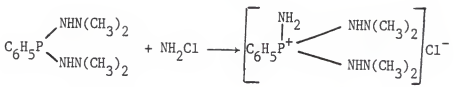
Chloramination of simple ditertiary phosphines[76] gives the double chloramination products. The reaction of chloramine with monohalophosphines yields $[R_2P(NH_2)_2]Cl$ or one of its condensation products.[70-73]

$$(C_6H_5)PCl + 2NH_3 + NH_2Cl \longrightarrow [(C_6H_5)_2P(NH_2)_2]Cl + NH_4Cl$$

$$\downarrow \Delta$$

$$(1/n)[(C_6H_5)_2PN]n + NH_4Cl$$

The reactions of chloramine with various substituted aminophosphines[54,78-82] and hydrazinophosphines[52,83-85] have indicated that the amino- or hydrazinonitrogens are not attacked by chloramine. It is, rather, the phosphorus atom that is the site of amination.



Chloramine reacts with several arsine derivatives to form chloramine adducts, which like the corresponding phosphine–chloramine adducts, condense to form arsenic–nitrogen chains.[76,86–89] Chloramine reacts with arsine, primary arsines, and secondary arsines to produce elemental arsenic, diarsines, and tetrasubstituted cyclopolyarsines, respectively[86] according to the general equation

$$zR_{3-x}AsH_x + (xz/2)H_2NCl \longrightarrow (R_{3-x}As)_z + (xz/2)NH_4Cl$$

Tertiary arsines, like tertiary phosphines, react with chloramine to give the respective aminoarsonium chlorides[52,76–88]

$$2(C_6H_5)_3As + 2NH_2Cl \longrightarrow 2[(C_6H_5)_3AsNH_2]Cl$$

$$\downarrow \Delta$$

$$[(C_6H_5)_3As{=}N{-}As(C_6H_5)_3]Cl + NH_4Cl$$

Various trialkylstibines and phenylstibines[90] react with chloramine. The initial amination product undergoes condensation in accordance with the equations

$$R_3Sb + NH_2Cl \longrightarrow R_3Sb(NH_2)Cl$$

$$2R_3Sb(NH_2)Cl \longrightarrow [R_3Sb(Cl)]_2NH + NH_3$$

Chloramine has been shown[91,92] to react with thiols, selenols, and a mixture of thiols and selenols with the extraction of the thiol or selenol hydrogen atom and the formation of disulfides, diselenides and selenosulfides, respectively, according to the equations

$$RXH + NH_2Cl \xrightarrow{X=S,Se} RXNH_2 + HCl$$

$$RXH + RXNH_2 \longrightarrow RXXR + NH_3$$

Chloramine can also act as a chlorinating agent. When a mixture of a gaseous olefin and chloramine is exposed to UV light or high temperature, hydrogen atoms on the olefin are replaced by chlorine.[93]

$$(CH_3)_2C{=}CH_2 \xrightarrow[NH_2Cl]{UV} (CH_3)_3CCl + CH_3\overset{\displaystyle CH_2}{\overset{\|}{C}}CH_2Cl + (CH_3)_2C(Cl)CH_2Cl$$

The photochemical addition of monochloramine to cyclohexene in ether at 0°C or 40°C results in the formation of trans-2-chlorocyclohexylamine, trans-1,2-dichlorocyclohexane, trans-2-chlorocyclohexanol, together with other products. The formation of these products was explained by a free radical mechanism.[94]

Experimental

All storing and transferring of amines and experimental purification work were conducted in a dry nitrogen atmosphere using a K.S.E. Model 2C 1982 gas purifier. All reactions were carried out in an atmosphere of prepurified nitrogen.

Diallylamine, obtained from the Aldrich Chemical Co., was refluxed and fractionated over solid KOH no more than two days before use and stored over a size 3A molecular sieve. The fraction boiling at 110-111°C was collected and used in the study. Triallylamine was obtained from Virginia Chemicals, Inc., and used as obtained.

Chloramine was prepared by the Sisler-Mattair process[50] and was used either as a gas or as its solution in ethyl ether. Figure 2.1 shows a diagram of the chloramine generator used in this work. Rotameters were

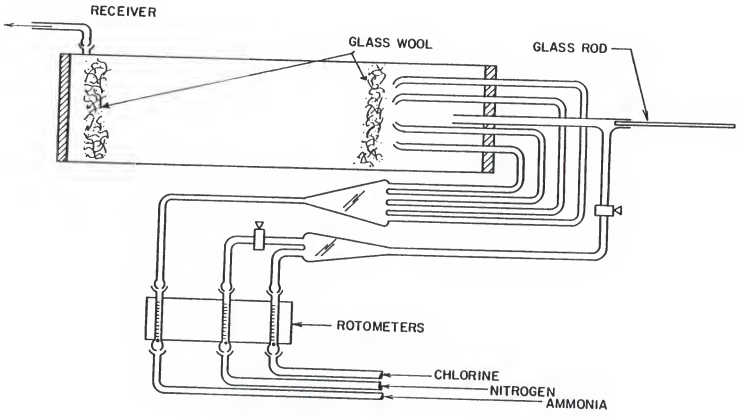


Figure 2.1. The chloramine generator.

used to measure the volume of gases and were adjusted to provide the following flow rates: ammonia, 1.2 mol/hr; nitrogen, 0.3 mol/hr; chlorine, 0.1 mol/hr. These rates provide a generation rate of chloramine of approximately 0.1 mol/hr.

$$2NH_{3(g)} + Cl_{2(g)} \longrightarrow NH_2Cl_{(g)} + NH_4Cl_{(s)}$$

Chloramine concentrations in the solutions were determined iodometrically by treating the sample with excess iodide and titrating the liberated iodine with sodium thiosulfate.

$$NH_2Cl + 2H^+ + 2I^- \longrightarrow NH_4^+ + I_2 + Cl^-$$

The following chemicals were obtained from the indicated suppliers: N_2, NH_3, Cl_2 (Matheson); $(CH_3)_2CO$ (Fisher, reagent); and used as obtained. The solvents CH_3CN and $CHCl_3$ (Fisher, ACS reagent) were dried by distillation over P_4O_{10}, ethyl ether, and benzene (Fisher, reagent) and were dried over sodium metal.

Analyses

Elemental analyses were done by Galbraith Laboratories, Inc., Knoxville, Tennessee. Melting points were obtained in sealed capillary tubes in a Thomas Hoover capillary melting point apparatus and are reported uncorrected.

Infrared Spectra

Infrared spectra were recorded on a Perkin-Elmer 283B infrared spectrophotometer. Solid samples were examined as KBr pellets or as Nujol mulls using sodium chloride plates. A summary of the IR data is found in Table 2.1.

Table 2.1

Infrared Absorption in cm^{-1} [a]

$[(CH_2{=}CH{-}CH_2)_2N(NH_2)_2]^+Cl^-$ (KBr)	3300-2800 (vs,multiple bands, 2030 (vw,d), 2000 (vw), 1930 (vw,d), 1715 (vw), 1660 (m,sh), 1645 (s), 1620 (s,sh), 1490 (vw), 1470 (vw), 1450 (s,d), 1420 (s), 1405 (w,sh), 1290 (m,d), 1210 (s,d), 1130-1040 (vs), 995 (vs), 950 (vs), 880 (m), 840 (s,d), 650 (s), 620 (vw,sh), 600 (vw,sh), 550 (m), 490 (s,d), 410 (m)
$[(CH_2{=}CH{-}CH_2)_3NNH_2]^+Cl^-$ (KBr)	3400 (m,b), 3300-2840 (vs,multiple bands), 2100 (vw,b), 1910 (vw), 1880 (vw,d), 1800 (vw), 1765 (vw), 1660-1540 (s,multiple bands), 1480-1390 (s,multiple bands), 1300 (vw), 1180 (vw), 1110 (m), 1040-900 (s,multiple bands), 865 (m), 835 (w), 775 (m), 685 (vw), 630-(w,d), 520 (w), 470 (m,b)

a b, Broad; d, doublet; m, medium; s, strong; sh, shsoulder; v, very; w, weak

Nuclear Magnetic Resonance Spectra

Proton NMR spectra were recorded on a Varian EM 360L NMR spectrometer or NT 300 Nicolet spectrometer. Carbon-13 and nitrogen-15 NMR measurements were made on a Nicolet 300 MHz multinuclear Fourier-transform NMR spectrometer.

Chloroform-d ($CDCl_3$) was used as the solvent and TMS as the internal reference. All chemical shifts are reported using the convention that a positive δ-value corresponds to a higher frequency chemical shift. The NMR spectral data are listed in Table 2.2.

Mass Spectra

Electron-impact mass spectra were obtained on an AEI MS-30 mass spectrometer operated at 70 eV and equipped with a DS-30 data system.

Reactions of the Chloramine-Ammonia Mixture with Diallylamine

The following experiments are illustrative:

(1). To a stirred solution of 0.08 mol of diallylamine in 35 mL of acetonitrile was added, over a 90 min period, 80 mL of an 0.24 M solution of chloramine in ethyl ether at 0°C. A white solid started to form. After allowing the reaction mixture to stand for 24 hr at 0°C, the reaction mixture was filtered. The solid was shown to be ammonium chloride (NH_4Cl). The volume of the filtrate was reduced to about 30 mL by a flow of nitrogen gas and/or by evacuation at 40°C. Ethyl ether was added to the remaining filtrate, and white crystals formed immediately. Melting points, IR, and ^1H NMR spectra showed that these crystals were diallylammonium chloride.

(2). Of a 0.24 M solution of chloramine in ethyl ether, 220 mL was added dropwise to a solution of 0.024 mol of diallylamine in 100 mL

Table 2.2

Nuclear Magnetic Resonance Data[a]

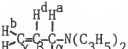
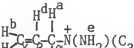
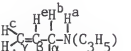
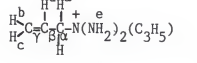
	^{1}H NMR			
	(ppm)	Assignment	J (Hz)	Relative Area Ratio
	3.031 (d)	a	H_aH_d = 6.40	6
	5.078 (d)	b	H_bH_d = 10.80	3
	5.129 (d)	c	H_cH_d = 19.91	3
	5.806 (m)	d	-	3
	4.256 (d)	a	H_aH_d = 7.13	6
	5.674 (d)	c	H_cH_d = 17.69	3
	5.687 (d)	b	H_bH_d = 9.53	3
	6.200 (m)	d	-	3
	6.631 (s)	e	-	2
	1.189 (s)	a	-	1
	3.196 (d)	b	H_bH_e = 5.95	4
	5.036 (d)	c	H_cH_e = 10.24	2
	5.141 (d)	d	H_dH_e = 17.205	2
	5.861 (m)	e	-	2

Table 2.2--extended

^{13}C NMR			^{15}N NMR		
δ (ppm)	Assignment	J (Hz)	δ (ppm)	Assignment	J (Hz)
56.128 (t)	α	J_{CH} = 134.15			
116.631 (t)	γ	J_{CH} = 155.74			
135.698 (d)	β	J_{CH} = 153.27			
65.868 (t)	α	J_{CH} = 146.53	-269.042 (t)	$-NH_2$	J_{NH} = 66.45
125.153 (d)	β	J_{CH} = 163.323	-286.775 (s)	N (quaternary)	-
128.150 (t)	γ	J_{CH} = 159.48			
50.447 (t)	α	J_{CH} = 132.94			
114.089 (t)	γ	J_{CH} = 155.95			
135.861 (d)	β	J_{CH} = 153.08			

Table 2.2--continued

	^{1}H NMR			
	(ppm)	Assignment	J (Hz)	Relative Area Ratio
	4.438 (d)	a	H_aH_d = 7.12	4
	5.584 (d)	c	H_cH_d = 17.12	2
	5.622 (d)	b	H_bH_d = 9.3	2
	6.113 (m)	d	-	2
	6.647 (s)	e	-	4

a d, Doublet; m, multiplet; s, singlet; t, triplet.

Table 2.2--extended

^{13}C NMR			^{15}N NMR		
δ (ppm)	Assignment	J (Hz)	δ (ppm)	Assignment	J (Hz)
68.678 (t)	α	J_{CH} = 143.20	-252.181 (t)	NH_2	J_{NH} = 65.87
125.165 (d)	β	J_{CH} = 162.26	-263.89 (s)	$N_{(quaternary)}$	-
126.792 (t)	β	J_{CH} = 158.12			

of acetonitrile at 0°C. The reaction mixture was stirred for 3 hr then kept in a refrigerator (0°C) for 24 hr. The reaction mixture was filtered; the solid was shown to be ammonium chloride (NH_4Cl). The filtrate was evaporated under vacuum at 20–50°C. White crystals were left which were shown to be diallylammonium chloride.

(3). The gaseous effluent from the chloramine generator was passed into 0.4 mol of neat diallylamine at 0°C for approximately 30 min; 50 mL of benzene was added to the reaction tube and chloramination was continued for another 60 min. As the NH_2Cl/NH_3 gas mixture was passed into the liquid amine, a white solid precipitated. After allowing the reaction mixture to stand overnight, the reaction mixture was filtered; the solid was washed three times with benzene (20 mL each) and dried under vacuum. The white solid was extracted first with 200 mL of acetone in four potions, then four times, 25 mL each, with acetonitrile, and finally with 75 mL of chloroform in three portions. The extracts in each case were combined and cooled in a water-ice bath for 24 hr. The shiny, white, cubic crystals formed in each solution were filtered, washed with ethyl ether, and dried. Ethyl ether was added to each filtrate to get as much solid as possible. The weight of the combined dry crystalline solid (mp 72–73°C; without decomposition) was 8.6 g, or 70% of theory, on the basis of the NH_2Cl used.

Anal. Calcd. for $[(CH_2{=}CH{-}CH_2)_2N(NH_2)_2]Cl$: C, 44.03; H, 8.62; N, 25.68; Cl, 21.66. Found: C,44.01; H, 8.44; N, 25.67; Cl, 21.70.

The filtrate from the original chloramination reaction mixture was found to reduce an acidified solution of potassium iodate to iodine, a qualitative as well as a quantitative test for hydrazines. However, attempts to isolate the hydrazine by fractional distillation led to a black polymeric material which was not identified.

The infrared spectrum, Figure 2.2, of the isolated solid does not show the two bands at about 3280 and about 750 cm^{-1} which are characteristic of the NH bond in secondary aliphatic amines. The spectrum also lacks the band at about 1840 cm^{-1} associated with the $RCH{=}CH_2$ out-of-plane bending. It does show a strong band at 950 cm^{-1} which is associated with quaternary ammonium salts. It also shows two bands at 840 and 880 cm^{-1} assigned to the $-NH_2$ group. Figure 2.3 shows, for comparison, the infrared spectrum of diallylamine.

The ^1H NMR spectrum of the compound is given in Figure 2.4. The peak at 4.438 is a doublet (J_{ad} = 7.12 Hz) and may be assigned to the protons on the α-carbon. The peaks at 5.584 and 5.632 ppm are two doublets (J_{cd} = 17.12 Hz, J_{bd} = 9.33 Hz) sharing one side and may be assigned to the protons on the γ-carbon; trans- and cis-, respectively. The multiplet peak centered at 6.113 may be assigned to the protons on the β-carbons. The sharp singlet at 6.647 is attributed to the $-NH_2$ protons. The ratio of the areas under the five peaks is 4:2:2:2:4, respectively. Figure 2.5 (a-c) shows, for comparison, the ^1H NMR spectrum of diallylamine.

The ^{13}C NMR spectrum, Figure 2.6 (a,b), consists of three peaks; the peak at δ = 68.678 is a triplet (J_{CH} = 143.20 Hz) and is attributed to the α-carbon atom. The two peaks at 125.165 and 126.792 are a doublet (J_{CH} = 162.26 Hz) and a triplet (J_{CH} = 158.12 Hz) and are assigned to the β- and γ-carbon atoms, respectively. The ^{13}C NMR spectrum of diallylamine is given in Figure 2.7 for comparison.

The ^{15}N NMR spectrum, Figure 2.8, shows two peaks: a singlet at δ = -263.89 ppm, and a triplet centered at δ = -252.181 ppm (J_{NH} = 65.865 Hz). The first peak is attributed to the quaternary nitrogen, and the second to the nitrogens of the $-NH_2$ groups.

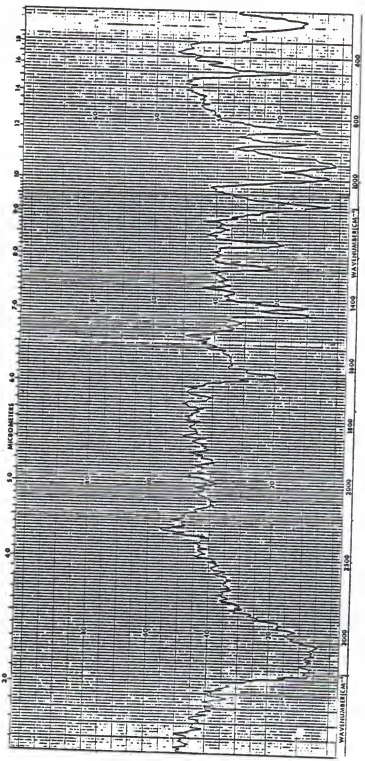


Figure 2.2. Infrared spectrum of 2,2-diallyltriazanium chloride.

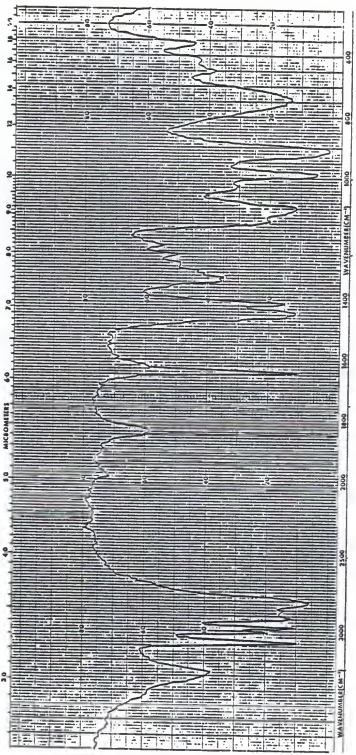


Figure 2.3. Infrared spectrum of diallylamine.

Figure 2.4. The 300 MHz ^{1}H NMR spectrum of 2,2-diallyltriazanium chloride in $CDCl_3$ solution.

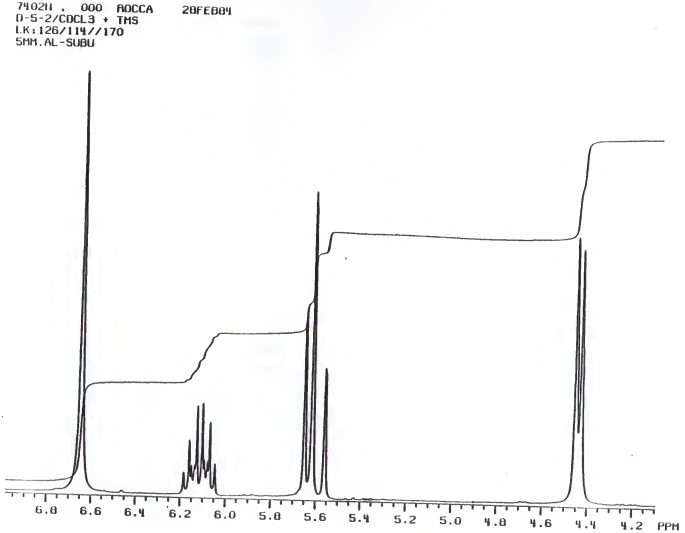
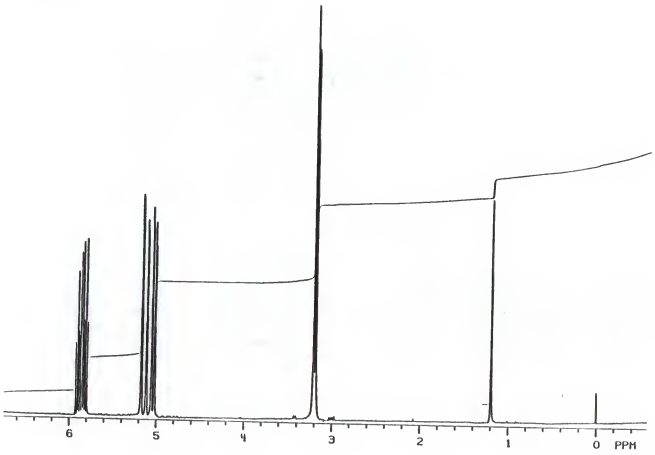
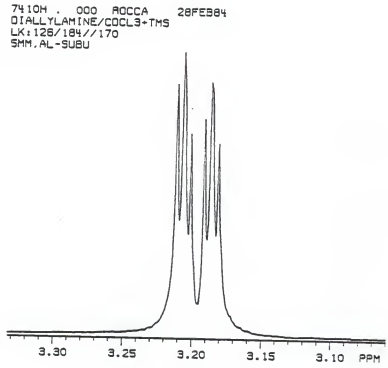

74021A . 000 ROCCA 20FEB04
D-5-2/CDCL3 + TMS
LK:126/114//170
5MM.AL-SUBU
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
PPM

Figure 2.5. (a) The 300 MHz ^{1}H NMR spectrum of diallylamine in $CDCl_3$ solution.


7410H . 000 ROCCA 20FEB84
DIALLYLAMINE/CDCL3+TMS
LK+126/184//170
5MM.AL-SUBU
6
5
4
3
2
1
0 PPM



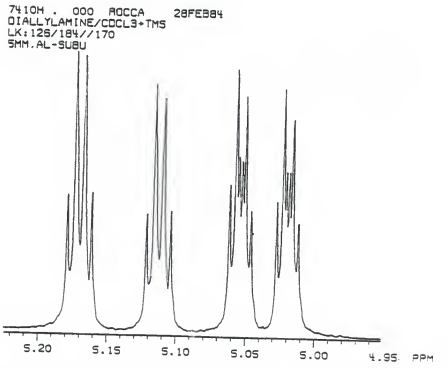


Figure 2.5 (continued). (b) The ^{1}H NMR spectrum of $H(C_{\alpha})$ and $H(C_{\gamma})$ in diallylamine, with expantion.

Figure 2.5 (continued). (c) The ^{1}H NMR spectrum of $H(C_{\beta})$ in diallylamine, with expansion.

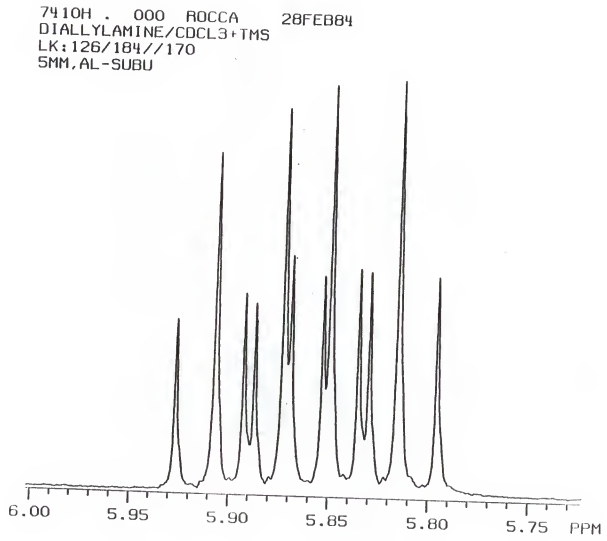

7410H . 000 ROCCA 28FEB84
DIALLYLAMINE/CDCL3+TMS
LK:126/184//170
5MM,AL-SUBU
6.00
5.95
5.90
5.85
5.80
5.75
PPM

Figure 2.6. The 300 MHz ^{13}C NMR spectrum of 2,2-diallyltriazanium chloride in $CDCl_3$ solution.

(a) Proton noise decoupled.

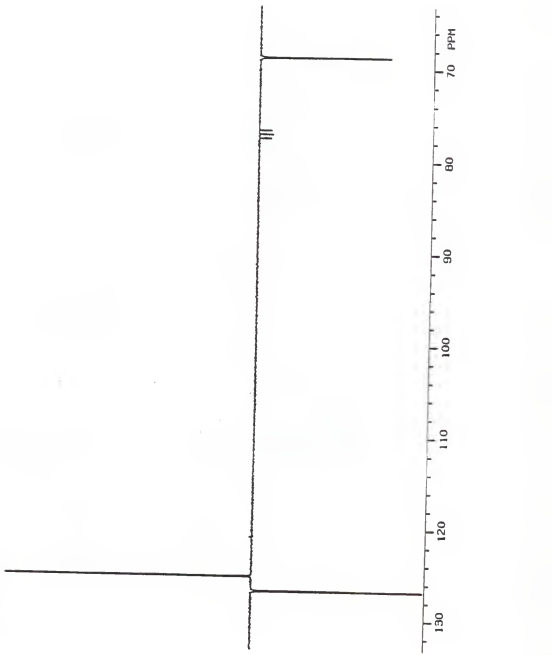
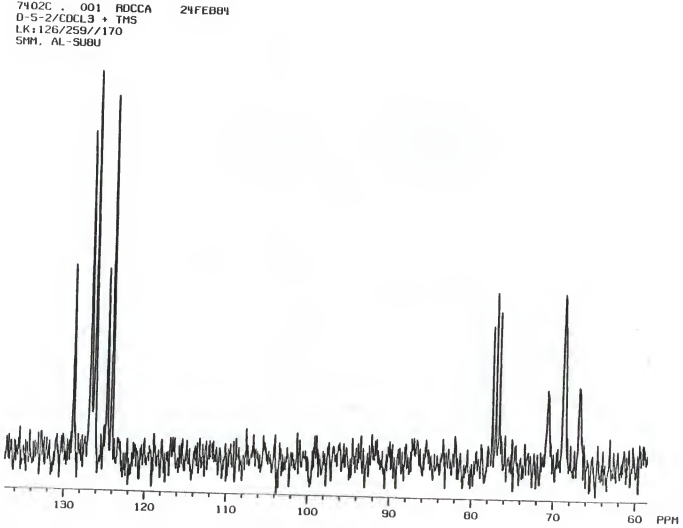

7402C , , 000 ROCCA 24FEB84
D-5-2/CDCL3 + TMS
LK:126/259/170
SAM, AL-SUBU
70
80
90
100
110
120
130
PPM

Figure 2.6 (continued). (b) The undecoupled ^{13}C NMR spectrum of 2,2-diallyltriazanium chloride.


7402C . 001 RDCCA 24FEB84
D-5-2/CDCL3 + TMS
LK:126/259//170
SMM. AL-SU8U
130
120
110
100
90
80
70
60
PPM

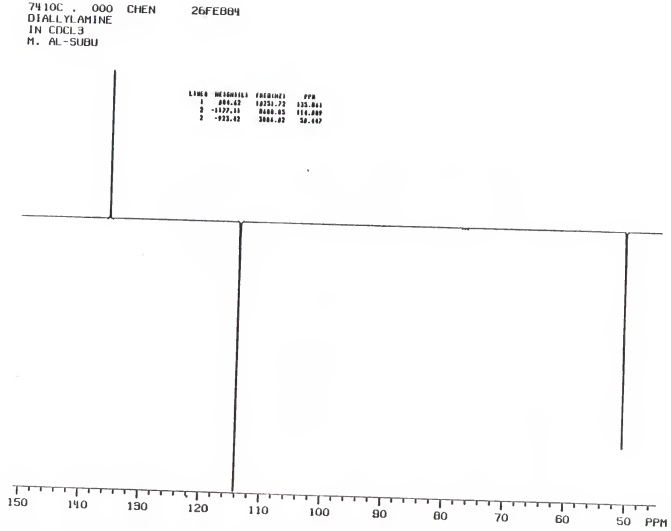


Figure 2.7. Proton noise decoupled 300 MHz ^{13}C NMR spectrum of diallylamine in $CDCl_3$ solution.

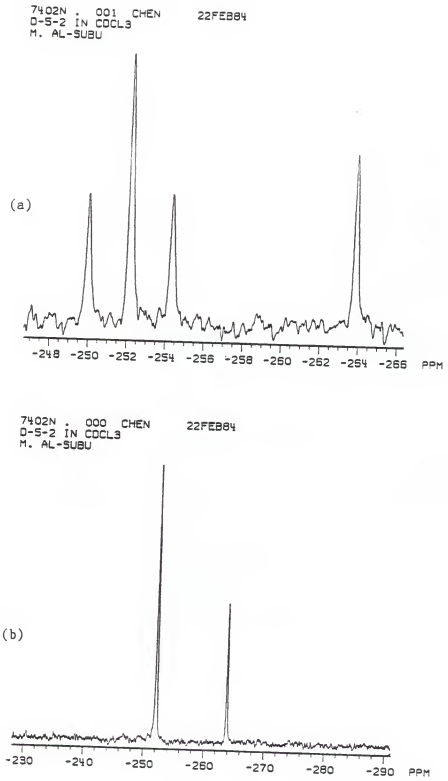


Figure 2.8. The 300 MHz ^{15}N NMR spectrum of 2,2-diallyltriazanium chloride in $CDCl_3$ solution: (a) proton noise undecoupled, (b) proton noise decoupled.

The mass spectrum, Figure 2.9, shows among other fragments, $(CH_2{=}CH{-}CH_2)_2N{=}N$ (m/e =110), $CH_2{=}CH{-}CH_2{-}NN$ (m/e = 69), $CH_2{=}CH{-}CH_2$ (m/e = 41), HCl (m/e = 36), and N_2 and/or $CH_2{=}CH_2$ (m/e = 28).

Reactions of the Chloramine-Ammonia Mixture with Triallylamine

(1). A 0.18 mol portion of neat triallylamine (bp 188.9°C) was treated with the effluent from the chloramine generator. As the chloramine-ammonia mixture was passed into the liquid amine, a light, white, gummy product formed. In about 40 min the product covered the whole surface of the reaction mixture. At that time a lot of fumes were evolved and a dark red solid and a dark solution obtained. Neither was investigated further. This experiment was repeated using anhydrous ethyl ether or benzene as solvent. In both these cases decomposition of the solid product in the reaction mixture was observed.

(2). In a typical reaction, chloramine from the chloramine generator was passed into 0.018 mol of triallylamine in 50 mL of acetonitrile over a 15-min period at room temperature. No apparent reaction took place in the initial stage. On standing overnight a white solid formed and was then filtered. The solid was found to be ammonium chloride. The filtrate was concentrated in vacuo to about 20 mL, and 40 mL of anhydrous ethyl ether added. A colorless oily layer separated at the bottom of the flask. The upper layer was decanted, the oil was washed with several portions of ethyl ether, dried in a vacuum desiccator and a deliquescent white solid was recovered. The deliquescent leaflets, after recrystallization from an ethyl ether-acetonitrile mixture (2:1 v/v) and drying, melted at 60-62°C; yield 2.1 g (62% of theory).

Anal. Calcd. for $[(CH_2{=}CHCH_2)_3NNH_2]Cl$: C, 57.28; H, 9.08; N, 14.84; Cl, 18.78. Found: C, 56.05; H, 9.00; N, 15.29; Cl, 18.88.

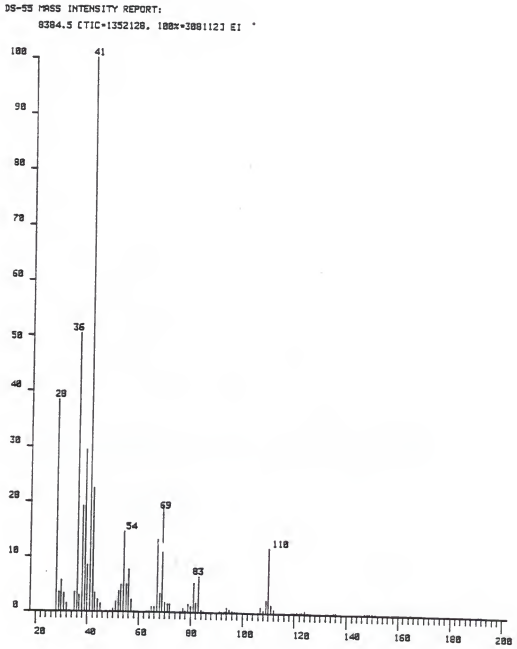


Figure 2.9. Mass spectrum of 2,2-diallyltrazanium chloride.

The infrared spectrum of the solid product is given in Figure 2.10. The spectrum lacks the absorption band at 1840 cm^{-1} associated with $RCH=CH_2$ out-of-plane bending. It shows two bands at 980 and 840 cm^{-1} characteristic of quaternary ammonium salts and associated with the $-NH_2$ group, respectively. Figure 2.11, for comparison, shows the infrared spectrum of triallylamine.

The ^1H NMR spectrum of the product is given in Figure 2.12. The peak at 4.256 ppm is a doublet (J_{ad} = 7.13 Hz) and is assigned to the protons on the α-carbon. The peaks at 5.674 and 5.687 ppm are two doublets (J_{cd} = 17.69 Hz, J_{bd} = 9.53 Hz) which overlap to give a triplet and are attributed to the protons on the γ-carbon, trans- and cis-, respectively. The multiplet peak centered at 6.200 is attributed to the protons on the β-carbons. The sharp singlet at 6.631 is attributed to the $-NH_2$ protons. The ratio of the areas under the five peaks is approximately 6:3:3:3:2, respectively. Figure 2.13 shows, for comparison, the ^1H NMR spectrum of triallylamine.

The ^{13}C NMR spectrum, Figure 2.14 (a,b), consists of three peaks; the peak at δ = 65.868 ppm is a triplet (J_{CH} = 146.53 Hz) and is attributed to the α-carbon atom; the two peaks at 125.153 and 128.150 are a doublet (J_{CH} = 163.23) and a triplet (J_{CH} = 159.48) overlap and are assigned to the β- and γ-carbon atoms, respectively. The ^{13}C NMR spectrum of triallylamine is given in Figure 2.15 (a,b) for comparison.

The ^{15}N NMR spectrum, Figure 2.16, shows two peaks: a singlet at δ = -269.042 ppm (J_{NH} = 66.48 Hz). The first peak is attributed to the quaternary nitrogen and the second to the nitrogen of the $-NH_2$ group.

Polymerization of 2,2-Diallyltriazanium Chloride

(1). Of the solid monomer 1.3 g was dissolved in 15 mL of acetonitrile; then the solution was diluted with acetonitrile in a 25 mL

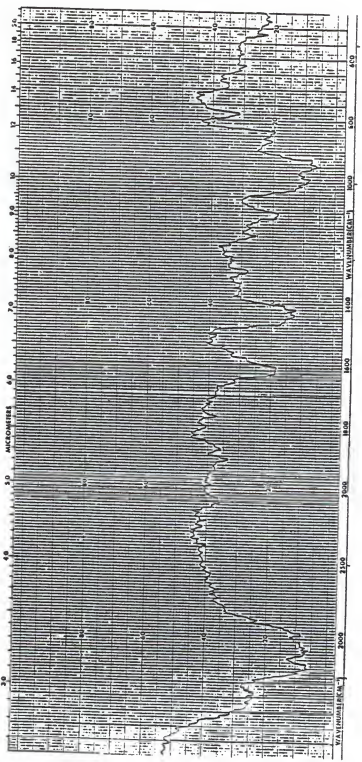


Figure 2.10. Infrared spectrum of 1,1,1-triallylhydrazanium chloride.

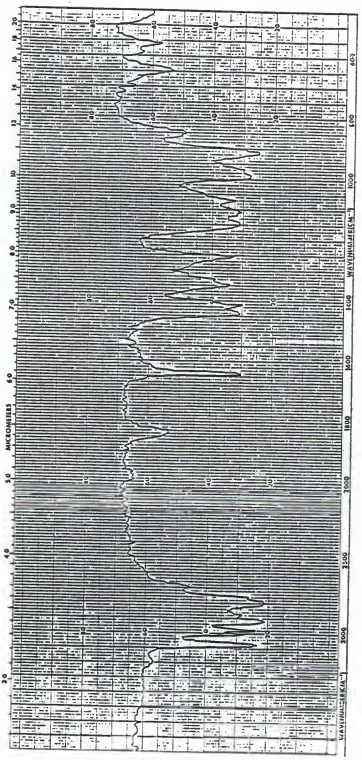


Figure 2.11. Infrared spectrum of triallylamine.

Figure 2.12. The 300 MHz ^{1}H NMR spectrum of 1,1,1-triallylhydrazinium chloride in $CDCl_3$ solution.

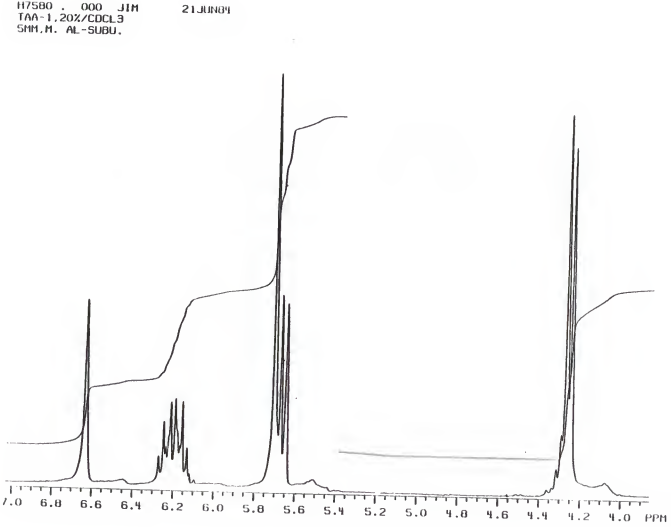

H7580 , 000 JIM 21JUN94
TAA-1.20%/CDCL3
5MM,M. AL-SUBU.
7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 PPM

Figure 2.13. The 300 MHz ^{1}H NMR spectrum of triallylamine in $CDCl_3$ solution.

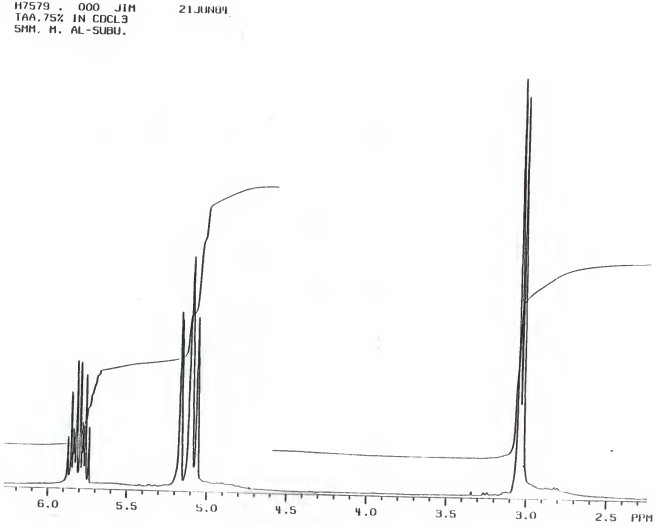

H7579 . 000 JIM 21JUN84
TAA,75% IN CDCL3
5MM. M. AL-SUBU.
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5 PPM

Figure 2.14. The 300 MHz ^{13}C NMR spectrum of 1,1,1-triallylhydrazinium chloride in $CDCl_3$ solution.

(a) Proton noise decoupled.

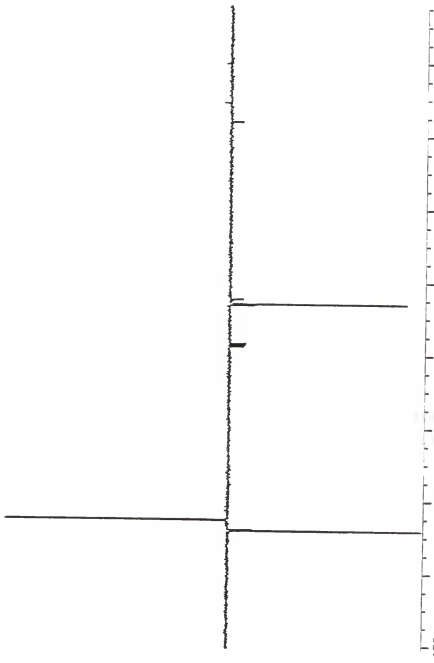

C7580 - 000 .1H 21JAN89
TMS,1.20X,CDCL3
SMM.M, AL-SUBU,
160
140
120
100
80
60
40
20
0
PPM

Figure 2.14 (continued). (b) The undecoupled ^{13}C NMR spectrum of 1,1,1-triallylhydrazinium chloride.

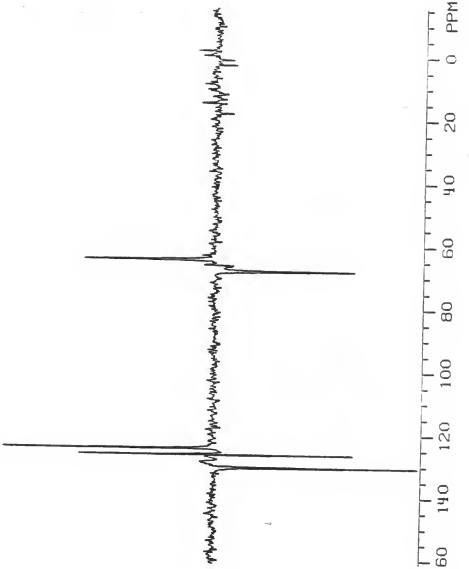

C7580 . 001 JIM 21JUN84
TAA-1.20%/CDCL3
5MM.M. AL-SUBU.
160 140 120 100 80 60 40 20 0 PPM

Figure 2.15. The 300 MHz ^{13}C NMR spectrum of triallylamine in $CDCl_3$ solution.

(a) Proton noise decoupled.

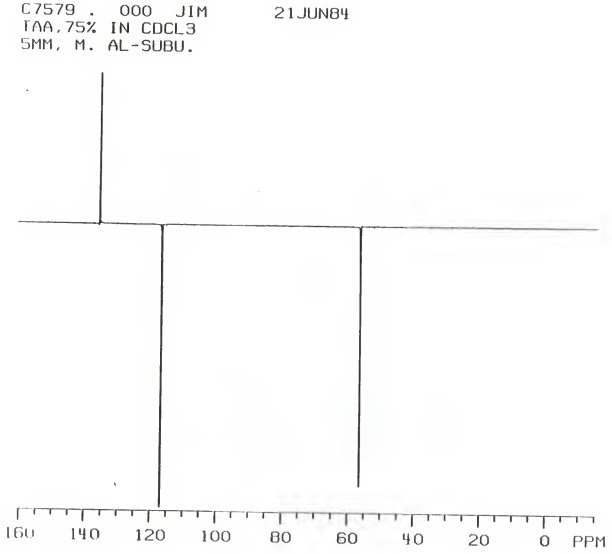
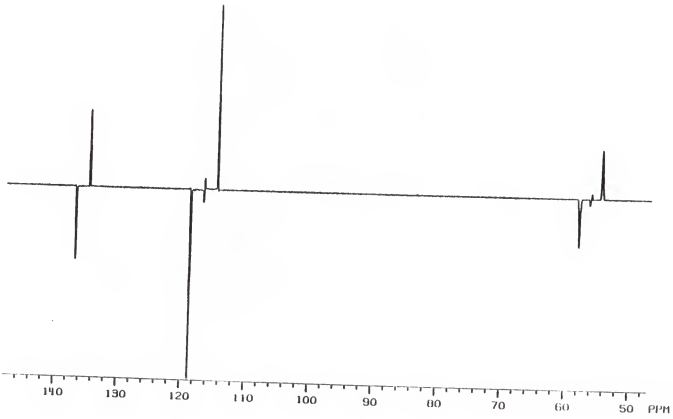

C7579 . 000 JIM 21JUN84
TAA,75% IN CDCL3
5MM, M. AL-SUBU.
160
140
120
100
80
60
40
20
0
PPM

Figure 2.15 (continued). (b) The undecoupled ^{13}C NMR spectrum of triallylamine.

C7579 . 001 JIM 21JUN84
1AA,75% IN CDCL3
5MM. M. AL-SUBU.



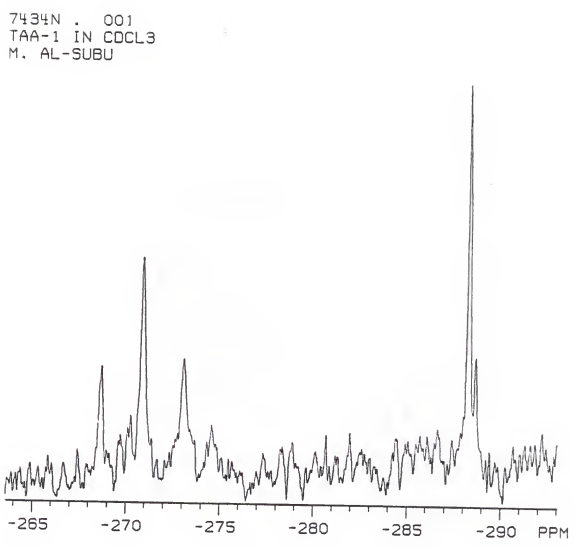


Figure 2.16. Proton noise undecoupled 300 MHz ^{15}N NMR spectrum of 1,1,1-triallylhydrazinium chloride in $CDCl_3$ solution.

volumetric flask. Five milliliters was pipetted out from the solution and transferred into a Pyrex test tube containing 1 mL of 0.016 M acetonitrile solution of AIBN (2,2'-azobisisobutyronitrile) as an initiator for the free radical reaction. To exclude oxygen and moisture, the solution was degassed by freezing with liquid nitrogen, evacuating the tube, closing the manifold stopcock, and allowing the material to warm to ambient temperature, this operation being carried out three times; then the tube was sealed and put in an oil bath regulated at 60°C to polymerize. After one week the tube was opened. This experiment was repeated using half the concentration of the monomer at 60°C. The above two experiments were repeated at 40°C. A brownish, water-insoluble polymer was obtained in each case, but in a low yield as most of the monomer was recovered by the addition of diethyl ether to the acetonitrile solution.

(2). In a 100 mL round flask under a nitrogen atmosphere, 1.0 g of 1,1-diallyltriazanium chloride, 2 mL of distilled water, and 10 µL of 70% t-butyl hydroperoxide were mixed well. The flask was placed in an oil bath regulated at 60°C. After two days a polymer was obtained as a light brown, granular solid. The polymer was removed and dried in an oven at 50°C under reduced pressure. The product (0.80 g) was insoluble in water, acetone, acetonitrile, benzene, chloroform, cyclohexane, diethyl ether, DMSO, DMF, n-hexane, methanol, methylene chloride, or petroleum ether. No further studies were carried out because of the lack of a suitable solvent.

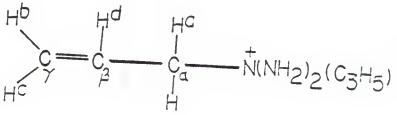
Discussion and Conclusions

This study has shown that chloramine reacts with diallylamine to form a compound that contains a high percentage of nitrogen and yet is

stable at its melting point. This compound has been identified as 2,2-diallyltriazanium chloride.

The infrared spectrum of the product is shown in Figure 2.2, and the spectral data are summarized in Table 2.1. Compared with the infrared spectrum of the parent amine (Figure 2.3), the spectrum of the product shows a new absorption band at 950 cm^{-1} which is associated with quaternary ammonium salts, and also shows two bands, at 840 and 880 cm^{-1}, which are assigned to the $-NH_2$ groups. However, but as expected, the spectrum lacks the two bands at about 3280 and 750 cm^{-1} which are characteristic of the N-H bond in secondary amines.

The proton NMR spectrum of the product (Figure 2.4 and Table 2.2) shows five types of protons in the compound with a relative area ratio of 4:2:2:2:4. The peak at δ 4.438 is a doublet with a proton-proton



coupling constant J_{ad} of about 7 Hz (lit 5-10 Hz); this peak is assigned to the protons on the α-carbon atoms. The two peaks at δ 5.583 and δ 5.632 are two doublets sharing the inter sides, and they are assigned to the protons on the γ-carbon atoms, trans- and cis-, respectively. The proton-proton coupling constants are J_{bd} about 9 Hz and J_{cd} about 17 Hz (lit ~18 and 12-24 Hz, respectively). The multiplet peak centered at δ 6.113 refers to the protons on the β-carbon atoms. The peak at δ 6.647 is a sharp singlet and is assigned to the $-NH_2$ protons. The same chemical shift for the $-NH_2$ protons is found in 1,1,1-triallylhydrazinium

chloride (~6.51), 2,2-dimethyltriazanium chloride (~6.7) and 1,1,1-trieth-ylhydrazinium chloride (~6.6) as will be seen later in this chapter and in Chapter 3. This might lead one to assume that the ^1H NMR chemical shift for the $-NH_2$ group on a quaternary nitrogen does not change from one compound to another. This point is worthy of further investigation.

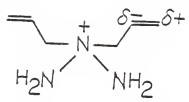
Compared with the ^1H NMR spectrum of diallylamine [Figure 3.5 (a-c)], the downfield shift in δ_H upon quaternization of the nitrogen atom [$\delta_{H(C_\alpha)}$ = 3.196 to 4.438 ppm; $\delta_{H(C_\beta)}$ = 5.861 to 6.113 ppm; $\delta_{H(C_\gamma)}$ = ~5.09 to ~5.60 ppm] is expected. Quaternization of the nitrogen atom results in a decrease in the electron density on the nitrogen, which has an electron withdrawing effect on all the carbon atom protons. The inductive effect of the quaternized nitrogen through the allyl group chain, as any other inductive effect through a molecular chain, weakens steadily with increasing distance from the quaternized nitrogen atom; this predicts the order of deshielding to be $H(C_\alpha) > H(C_\beta) > H(C_\gamma)$. However, a closer look at the values of the downfield shifts for the protons shows that the order of $H(C_\beta)$ and $H(C_\gamma)$ is reversed: $H_{(C_\alpha)}$ (1.24 ppm) > $H_{(C_\beta)}$ (~0.25 ppm) < $H_{(C_\gamma)}$ (~0.52 ppm). This reversal also is worthy of further investigation.

The ^{13}C NMR spectrum of the product is shown in Figure 2.6 (a,b), and the spectral data are summarized in Table 2.2. The spectrum shows three peaks for the carbon atoms in the compound. The triplet centered at δ 68.678 with a carbon-proton coupling constant $^1J_{CH}$ of about 143 Hz is assigned to the α-carbon atom (lit J_{CH} in $CH_3NH_3^+$ = 145 Hz). The peak at δ 125.165 is a doublet, $^1J_{CH}$ of about 162 Hz and is assigned to the β-carbon atom. The third peak is another triplet centered at δ 126.792, $^1J_{CH}$ of about 158 Hz and is assigned to the γ-carbon atom.

The ^{13}C NMR spectrum of the parent compound (diallylamine) is shown in Figure 2.7, and the data are summarized in Table 2.2. Comparison between the spectrum of diallylamine and 2,2-diallyltriazanium chloride shows that quaternization of the central nitrogen causes a downfield shift of the chemical shift of the α-carbon atom by about 18 ppm (δ 50.447 to δ 68.678) and that of the γ-carbon atom by about 13 ppm (δ 114.089 to δ 126.792). At the same time, it causes an upfield shift of the β-carbon by about 9 ppm (δ 135.861 to δ 126.792).

A substituent in the α- or β-position generally deshields the carbon nucleus (downfield shift) but on the γ-position is shielding (upfield shift). This is known as γ-effect[95] and has been interpreted as a steric shift. The electron withdrawing effect of the quaternary nitrogen through the allyl group chain would also predict a deshielding of the three carbon atom nuclei in the decreasing order $C_\alpha > C_\beta > C_\gamma$. However, re-examining the ^{13}C NMR data shows that the above two theories explain only the downfield shift of C_α but not the upfield shift of C_β (~9 ppm) or the downfield shift of C_γ (13 ppm). Also, the γ-effect does not explain why $H(C_\gamma)$ is shifted twice as much as $H(C_\beta)$ in the ^1H NMR spectrum of 2,2-Diallyltriazanium chloride. The following explanation is offered for both the ^1H NMR and ^{13}C NMR spectra.

The structure of 2,2-diallyltriazanium cation might be described in a way similar to that of 2,2-dimethyltriazanium cation which was determined by x-ray diffraction.[65] The cation is assumed to consist of a central nitrogen surrounded tetrahedrally by two amino and two allyl groups. Quaternization of the nitrogen atom develops a positive charge on that nitrogen. The $-NR(NH_2)_2$ group may be viewed as a substituent on the allyl group which polarizes the π-electron density of the double bond either through the allyl group bonds or through space. This polarization



increases the electron density at the β-carbon which causes an upfield shift in δ_{C_β} and a smaller downfield shift in $\delta_{H(C_\beta)}$. The polarization has an opposite effect on C_γ by reducing the π electron density resulting in a downfield shift in δ_{C_γ} and a larger downfield shift in $\delta H(C_\gamma)$.

The ^{15}N NMR spectrum, Figure 2.8, shows two peaks, a triplet centered at about δ = -252 ppm and a singlet at about δ = -263 ppm from nitromethane as an internal reference. The triplet is twice the intensity of the singlet with a nitrogen-proton coupling constant $^1J_{NH}$ of about 66 Hz and is assigned to the amino nitrogens. The singlet is assigned to the quaternary nitrogen atom. Similar values of nitrogen-proton coupling constant are obtained for 1,1,1-triallylhydrazinium chloride ($^1J_{NH}$ ~ 66 Hz) and 2,2-dimethyltriazanium chloride (J_{NH} = 66 Hz) as will be seen later in this chapter and in Chapter 3. This value of nitrogen to proton spin-spin coupling of $-NH_2$ group on a quaternized nitrogen might be used for structure elucidation.

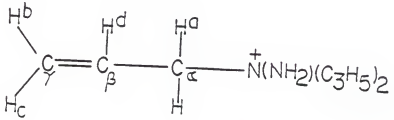
The mass spectrum of 2,2-diallyltriazanium chloride (Figure 2.9) shows among other fragments, $(CH_2{=}CH{-}CH_2)_2NN$ (m/e 110), $CH_2CH{-}CH_2NN$ (m/e 69), $CH_2{=}CH{-}CH_2$ (m/e 41), HCl (m/e 36), and N_2 and/or $CH_2{=}CH_2$ (m/e 28). No fragmen ation scheme is proposed.

The second purpose of this work was to study the reaction between chloramine and triallylamine. The experimental results show that this

reaction, under the proper conditions, proceeds to give 1,1,1-triallyl-hydrazinium chloride.

The infrared spectrum of the product and that of the parent amine are shown in Figure 2.10 and 2.11, respectively. The spectrum of the product showed a new absorption at about 980 cm^{-1} which is characteristic of quaternary ammonium compounds. The spectrum shows another new peak around 840 cm^{-1} which is associated with the $-NH_2$ group.

The proton NMR spectrum, Figure 2.12, is summarized in Table 2.2. The spectrum shows five peaks for the product, a doublet at δ 4.256 with a proton-proton coupling constant J_{ad} of about 7 Hz and is assigned to the protons on the α-carbon atom. The two doublets at δ 5.674



(J_{cd} ~ 18 Hz) and δ 5.687 (J_{bd} ~ 10 Hz) overlap to give what looks like a triplet and are assigned to the protons on the γ-carbon, trans- and cis-, respectively. The fourth peak is a multiplet and is assigned to the protons on the β-carbon atom. The protons of the amino group constitute the fifth peak which appears in the spectrum as a sharp singlet at δ 6.631 ppm. The ratio of the areas under the five peaks is consistent with the assignment, and it is approximately 6:3:3:3:2.

Similar trends to those found in the case of 2,2-diallyltriazanium chloride are noticed here when the ^1H NMR spectrum of 1,1,1-triallyl-hydrazinium chloride is compared with the ^1H NMR spectrum of

triallylamine (Figure 2.13): A downfield shift for all protons along the allyl group chain is noticed upon quaternization of the nitrogen atom [$\delta_{H(C_\alpha)}$ from 3.031 to 4.256 ≃ 1.23 ppm; $\delta_{H(C_\beta)}$ from 5.806 to 6.200 ≃ 0.39 ppm; $\delta_{H(C_\gamma)}$ from ~5.1 to ~5.7 ≃ 0.58 ppm. The downfield shift is expected to result from the electron withdrawing effect of the quaternized nitrogen. The relative values of the chemical shift changes of the various hydrogens on the allyl group carbon chain when going from the amine to the hydrazinium chloride might be explained in a manner similar to the case of 2,2-diallyltriazanium chloride.

The ^{13}C NMR spectrum of the product is shown in Figure 2.14 (a,b), and the spectral data together with those of triallylamine are summarized in Table 2.2. The spectrum consists of three peaks: a triplet centered at δ 65.868 with a carbon-proton coupling constant $^1J_{CH}$ of about 147 Hz and is assigned to the α-carbon atom; the second peak δ 125.153 is a doublet $^1J_{CH}$ of about 163 Hz and is assigned to the β-carbon atom; the third peak δ 128.150 is a triplet $^1J_{CH}$ of about 160 Hz and is assigned to the γ-carbon atom. The second and third peaks share an edge as shown in Figure 2.14b.

Once again, comparing the ^{13}C NMR spectrum of 1,1,1-triallylhydrazinium chloride with that of triallylamine [Figure 2.15 (a,b) , it is noticed that the quaternization of the nitrogen atom is accompanied by a downfield shift in the chemical shifts of C_α and C_γ by about 10 and 12 ppm, respectively, and an upfield shift in the chemical shift of C_β by about 11 ppm. This situation is similar to that observed previously in 2,2-diallyltriazanium chloride ^{13}C NMR spectrum, and it might be explained similarly by assuming a polarization of the double bond π electron by the quaternized nitrogen.

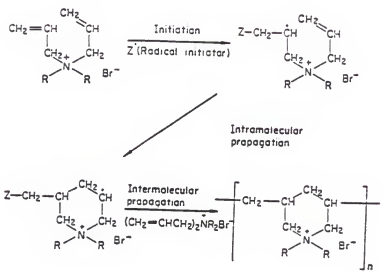
The ^{15}N NMR spectrum, Figure 2.16, shows two types of nitrogen atoms in the compound: a singlet at $\delta \simeq -289$ and a triplet at $\delta \simeq -269$ ppm from nitromethane as internal reference. The two peaks are assigned to the quaternary nitrogen and the amino nitrogen, respectively. The nitrogen to hydrogen spin-spin coupling constant in the triplet is about 66 Hz which is about the same as the $^{1}J_{NH}$ values found in similar compounds mentioned earlier.

The third purpose of this work was to check on the polymerization of 2,2-diallyltriazanium chloride. It is found in this study that when 2,2-diallyltriazanium chloride is mixed in water with a very small amount of t-butyl hydroperoxide as a free radical initiator, a light brown colored solid is obtained. The product is insoluble in water, and it is also insoluble in several other solvents of various dielectric constants such as methanol, methylene chloride, DMSO, DMF, acetonitrile, acetone, chloroform, diethyl ether, cyclohexane, benzene, n-hexane, and petroleum ether. The low solubility of the product in that wide range of solvents is a well-known behavior of cross linked polymers; this suggests that 2,2-diallyltriazanium chloride is polymerized in the presence of t-butyl hydroperoxide to give a cross linked polymer.

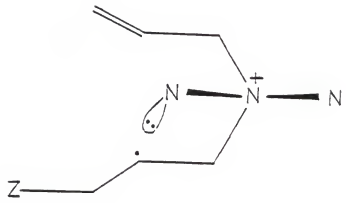
$$n[(C_3H_5)_2N(NH_2)_2]^+Cl^- \xrightarrow[\text{hydroperoxide}]{\text{t-butyl}} [(C_3H_5)_2N(NH_2)_2Cl]_n$$

Quaternary ammonium salts having three or four allyl groups are known to polymerize via a free radical mechanism to produce water-insoluble materials.[96] However, extensive studies of the polymerization of ammonium salts having two allyl groups and two other saturated alkyl groups such as methyl groups, showed that the polymerization via free radical mechanism results in the production of water-soluble

cyclopolymers containing five- and six-membered rings[97] as shown by the following polymerization mechanism (only the formation of six-membered rings is shown):



Giordano et al.[65] reported that the structures of 2,2-dimethyltriazanium- and tetramethylammonium cations are quite similar. By analogy, 2,2-diallyltriazanium- and diallyldimethylammonium cations may have similar structures. Therefore, the formation of a cross linked polymer in the case of 2,2-diallyltriazanium chloride rather than a cyclopolymer as for diallyldimethylammonium chloride may result from the presence of amino groups rather than resulting from structural differences around the quaternary nitrogen, and, in particular, resulting from the unshared pair of electrons on each amino nitrogen. The structure of the radical produced in the initiation step may be redrawn as



There is repulsion between the unshared pair of electrons on the amino nitrogen and the odd electron which may inhibit intramolecular propagation and enhance directly or indirectly the intermolecular propagation.

One might argue that the cross linked polymerization is a result of the high concentration of the monomer in the reaction mixture (1.0 g in 2.0 mL H_2O); this possibility is not probable, however, because a) if the concentration is the only factor, one would expect to get both types of polymerization whereas the yield of the cross linked polymer is almost quantitative with no indication of the formation of the cyclopolymer; b) when the polymerization was carried in dilute solutions of acetonitrile (as low as 0.25 g in 20 mL), and only a very small amount of the polymer was obtained over a seven-day period, the polymer was, nevertheless, cross linked. The remaining material was recovered from the solution and identified by its melting point, ^1H NMR, and ^{13}C NMR as starting material.

Compared with other known triazanium chlorides, 2,2-diallyltriazanium chloride has some unique properties:

1) 2,2-Diallyltriazanium chloride is the first triazanium chloride prepared with unsaturated alkyl group substituents.

2) It has the lowest melting point of known triazanium chlorides and is the first known triazanium chloride to melt without decomposition.

3) On being heated, 2,2-diallyltriazanium chloride ignites much more readily than other known triazanium chlorides.

4) It is the first triazanium chloride that can be polymerized. This polymer may be the first polymer that contains three nitrogen atoms in a singly bonded chain in its repeating unit.

The 1,1,1-triallylhydrazinium chloride, 2,2-diallyltriazanium chloride, and its polymer may find applications, especially in those areas that require "high-energy" compounds such as components of solid rocket fuels. Also, 1,1,1-triallylhydrazinium and 2,2-diallyltriazanium chlorides may be used to form a variety of copolymers.

Summary

The products of the reactions of chloramine with diallyl- and triallylamines were found to be 2,2-diallyltriazanium chloride and 1,1,1-triallylhydrazinium chloride, respectively. In both compounds, quaternization of the nitrogen atom results in a downfield shift of all ^{1}H NMR chemical shifts in the order $H(C_\alpha) > H(C_\gamma) > H(C_\beta)$. Carbon-13 NMR chemical shifts are also shifted, downfield for C_α and C_γ and upfield for C_β. The changes in the chemical shifts were explained by assuming a polarization of the π-electron bond of the double bond by the positively charged quaternary nitrogen.

It was found that 2,2-diallyltriazanium chloride undergoes a radical initiated polymerization to yield a cross linked polymer which is insoluble in a wide variety of solvents. The formation of the

polymer as a cross linked rather than a cyclopolymer was explained as resulting from the repulsion between the unshared pair of electrons on the amino nitrogen and the odd electron produced on the β-carbon by the initiator.

Some of the properties and possible applications of the three new compounds are discussed.

CHAPTER THREE

A STUDY OF THE EFFECT OF 18-CROWN-6 ON THE CHLORAMINATION OF 1,1-DIMETHYLHYDRAZINE

Introduction

Compounds that have a high percentage of nitrogen have found applications in those areas requiring "high-energy" chemicals, such as solid propellants, explosives, and the like. Representative of such materials that possess high nitrogen content are the hydrazines and their salts.

Before 1966, no stable alkyl compounds which contain a single bonded chain of more than two nitrogen atoms were known except for a brief note by Gösl.[98] Gösl reported the formation of a dialkyltriazanium salt by the reaction of 1,1-dimethylhydrazine with hydroxylamine-O-sulfonic acid in methanol. In this report, however, no experimental conditions nor analytical data supporting its formation were described.

In 1966 and subsequently, Utvary and Sisler, through the use of chloramination reactions, have reported in a series of more detailed papers the synthesis of a number of 2,2-dialkyltriazanium salts.[59,60,99-102] These authors have shown unequivocally that chloramine, as an electrophile,[54-56] reacts at the more basic nitrogen atom of unsymmetrically substituted hydrazines, the one containing the alkyl groups.

Some crown ethers of proper cavity size are known to assist nucleophilic reactions by acting as catalysts.[103-108] Some crown ethers were applied to amination and amino acid synthesis. For example,

the presence of catalytic amounts of 18-crown-6 benzylchloride is converted to the acetoamide derivative by the reaction of Na acetoamide.

A specific object of this study was to provide a method for producing 2,2-dimethyltriazanium chloride in higher purity and higher yield by the reaction of chloramine with 1,1-dimethylhydrazine in the presence of a catalytic amount of the 18-crown-6 ether. Chloramine is an unstable chemical and may not be stored. Therefore, an additional object of the present study was to determine if the 18-crown-6 ether forms a stable adduct with chloramine, as it does with many ionic and polar organic compounds, and if so, whether or not this adduct could be used as a source of chloramine in chloramination reactions.

Historical Background

Methods of Synthesizing Triaznium Salts

Over the past two decades, reports have appeared concerning the preparation of simple dialkyl substituted triazanium salts $[NH_2NR_2NH_2]Cl$. Synthesis of triazanium salts is based on amination reactions by such reagents as hydroxylamine-O-sulfonic acid, chloramine-ammonia mixtures, and 2-acyloxazirides. Here briefly is a summary of these reactions.

(1) Hydroxylamine-O-sulfonic acid. To synthesize salts with the $[(CH_3)_2N(NH_2)_2]^+$ cation, one usually uses the amination of 1,1-dimethylhydrazine with hydroxylamine-O-sulfonic acid or its Na salt.[98] According to Equation 1, 2,2-dimethyltriazanium sulfate is formed.

$$4(CH_3)_2NNH_2 + 2H_2NOSO_2OH \xrightarrow{CH_3OH} [(CH_3)_2N(H)(NH_2)]_2^+SO_4^{2-} + [(CH_3)_2N(NH_2)_2]_2^+SO_4^{2-} \qquad (1)$$

(2) Chloramine-ammonia mixture. (a) Chloramination of secondary aliphatic amines in the presence of ammonia yields the corresponding 2,2-dialkyltriazanium chlorides according to the Equations 2 and 3.[59,60,63,66,102]

$$RR'NH + 2NH_2Cl + NH_3 \longrightarrow [RR'N(NH_2)_2]^+Cl^- + NH_4Cl \qquad (2)$$

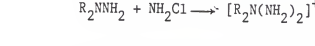
$$2RR'NH + 2NH_2Cl \longrightarrow [RR'N(NH_2)_2]^+Cl^- + RR'NH_2Cl \qquad (3)$$

R, R' = me, et, pr, bu, and/or benzyl group

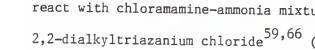
(b) The reaction of chloramine with 1,1-dialkylhydrazines:[59,60,63,100,102] 2,2-dialkyltriazanium chlorides are most conveniently prepared by the reaction of chloramine with unsymmetrical dialkylhydrazines (Equation 4).

$$R_2NNH_2 + NH_2Cl \longrightarrow [R_2N(NH_2)_2]^+Cl^- \qquad (4)$$

(c) 2-dialkylamino- and 2-(N,N-dimethylhdrazino-1,3,2-dioxophospholanes react with chloramamine-ammonia mixtures to produce the corresponding 2,2-dialkyltriazanium chloride[59,66] (Equations 5 and 6).



(5)



(6)

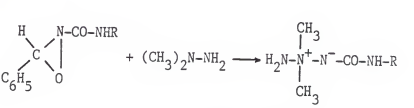
(d) The compound 2,2-dimethyltriazanium chloride is obtained by the cleavage of X-N bond (X = Si, Ge or Sn) in the reaction of chloramine with certain silyl-, germyl-, and stannylamines.[110] An example is shown in Equation 7.

$$(CH_3)_3Sn\text{-}N(CH_3)_2 + 2NH_2Cl \longrightarrow (CH_3)_3SnCl + [(CH_3)_2N(NH_2)_2]^+Cl^- \quad (7)$$

(e) Giordano and Sisler[61] have obtained 2,2-dimethyltrazanium chloride from the trimethylhydrazine-chloramination reaction mixture (Equation 8).

$$(CH_3)_2NNH(CH_3) + NH_3 + NH_2Cl \longrightarrow [(CH_3)_2N(NH_2)_2]^+Cl^- + CH_3NH_2 \quad (8)$$

(3) 2-Acyloxaziridines. Triazanium salts with one unsubstituted amino group produced by amination of 1,1-dimethylhydrazine with 2-acyloxaziridines have been reported.[111] The formation of the salt appears to follow Equation 9.



$$R = H,\ C_6H_5$$

(9)

In addition to dialkyl-substituted triazanium chlorides and sulfates, the synthesis of several 2,2-dimethyltriazanium salts having other anions have been reported.[102] The bromide, -iodide, -methylsulfonate, -nitrate, -perchlorated and -toluolsulfonated have been prepared by reaction of 2,2-dimethyltriazanium chloride with the appropriate silver salts in methanol or with potassium halides in liquid ammonia.[102]

Structure and Stability

The structural formula of 2,2-dimethyltriazanium chloride is $[(CH_3)_2N^+(NH_2)_2]Cl^-$, as was determined by x-ray diffraction.[65] The cation consists of a central nitrogen surrounded tetrahedrally by two amino and two methyl groups. In the crystal, the chloride ion is bonded to the cation by hydrogen bonds through the amino hydrogens.

Dimethyltriazanium salts, though less stable than analogous tetramethylammonium salts,[112] are stable in air and neutral aqueous solution and can be recrystallized from boiling solvents such as acetone, acetonitrile, ethanol and ether. The stability is suggested to result from the quaternization of the central nitrogen atom.

Thermochemical Properties

Thermochemical data for the $[(CH_3)_2N(NH_2)_2]^+$ cation and its nitrate and perchlorate salts have been reported[112] and are shown in Table 3.1.

Table 3.1

Thermochemical Data for $[(CH_3)_2N(NH_2)_2]^+$ and Its Salts

	$(CH_3)_2N(NH_2)_2^+$	$[(CH_3)_2N(NH_2)_2]^+NO_3^-$	$[(CH_3)_2N(NH_2)_2]^+ClO_4^-$
$\Delta H_c°$ kcal mol^{-1}	-	-404.86±.21	-
ΔH_r kcal mol^{-1}	-	9.540±0.015	10.08±0.02
$\Delta H_f°$ kcal mol^{-1}	24.29±0.24	-33.82±0.21	-16.66±0.25

$\Delta H_c°$: enthalpy of combustion
ΔH_r: enthalpy of dissolution in water
$\Delta H_f°$: enthalpy of formation

Experimental

Materials

The compound 1,1-dimethylhydrazine was obtained from the Rocky Mountain Arsenal and was refluxed and distilled over solid KOH and stored at 0°C. The compound 18-crown-6 ether (99%) was obtained from Aldrich Chemical Co. and used as received. Triethylamine (Eastman Kodak,

practical grade) was refluxed over calcium hydride, then distilled from it under dry nitrogen, and stored over metallic sodium. The following solvents were obtained from the indicated suppliers: anhydrous diethyl ether (Fisher, certified ACS), acetonitrile (Kodak, spectra grade), chloroform (Fisher Scientific, spectra grade).

Chloramine, produced by the gas phase reaction of ammonia and chlorine using a generator similar to that described by Sisler et al.,[113] was collected in cooled diethyl ether. Ammonia was allowed to evaporate as the volume of ether was reduced to give a concentrated solution of chloramine. Dimethylchloramine and monomethylchloramine were prepared by a procedure analogous to the Raschig synthesis of chloramine.[113] The pure dimethylchloramine (bp 43°C) was then diluted with diethyl ether to give the solution used in the experiment. Monomethylchloramine was extracted with diethyl ether and dried over anhydrous potassium carbonate.

Chloramine, monomethylchloramine, or dimethylchloramine contents of the solutions were determined before each experiment by allowing aliquot samples of the chloramine solution to react with acidified potassium iodide solution, the iodine released being titrated with a standard sodium thiosulfate solution.

Analyses

Elemental analyses were done by Galbraith Laboratories, Inc., Knoxville, Tennessee. Melting points were obtained in sealed capillary tubes in a Thomas-Hoover capillary melting point apparatus and are reported uncorrected.

The infrared spectra were recorded on a Perkin-Elmer 283B infrared spectrophotometer. Solid samples were examined as KBr pellets. A summary of the IR data is found in Table 3.2.

Table 3.2

Infrared Absorption in cm^{-1} [a]

$[(CH_3)_2N(NH_2)_2]^+Cl^-$ (KBr)	3230 (vs), 3130 (vs), 3030 (s), 2950 (m), 2890 (m), 1620 (s), 1455 (m), 1415 (w), 1395 (w), 1285 (s), 1230 (m), 1155 (m), 1095 (vs), 1075 (s,sh), 955 (w), 930 (s), 885 (m), 860 (s), 740 (w), 525 (m), 485 (m), 435 (m)
18-crown-6 ether·NH_2Cl (KBr)	3450 (b,m), 3150 (b,m), 2890 (m), 2820 (vw), 1650-1560 (w), 1460 (b,s), 1395 (s), 1350 (s), 1275 (m), 1245 (m), 1230 (sh), 1105 (vs), 965 (vs), 835 (s)
$[(CH_3CH_2)_3NNH_2]^+Cl^-$ (KBr)	3200 (s), 3090 (s), 3050 (w,sh), 2985 (w), 2940 (vw), 1620 (m), 1560 (w,sh), 1480 (s), 1445 (m), 1395 (m), 1350 (vw,sh), 1195 (m), 1150 (s), 1085 (s), 990 (s), 920 (s), 875 (m), 800 (s), 775 (m), 770 (vw), 550 (m), 480 (s), 435 (s)

a b, Broad; d, doublet; m, medium; s, strong; sh, shoulder; v, very; w, weak.

Nuclear Magnetic Resonance Spectra

A Nicolet 300 MHz multinuclear Fourier-Transform NMR spectrometer was used to record ^{1}H, ^{13}C and ^{15}N NMR spectra. Chloroform-d or dimethyl sulfoxide-d6 was used as the solvent with tetramethylsilane (TMS) as the internal reference for ^{1}H and ^{13}C spectra and nitromethane as the internal reference for ^{15}N spectra. The NMR spectral data are listed in Table 3.3.

The Reaction of 1,1-Dimethylhydrazine with Chloramine in the Presence of the Crown Ether 18-Crown-6

In a typical experiment, 95 mL of a solution of chloramine in diethyl ether (0.14 M) was added to a solution of 1,1-dimethylhydrazine (1.0 mL, 13 mmol) and 18-crown-6 ether (0.50 g, 1.9 mmol) in 50 mL of diethyl ether with stirring at 0°C. The reaction occurred immediately with the formation of a white precipitate. The reaction mixture was stirred overnight, then filtered under nitrogen, washed first with 25 mL diethyl ether then with 50 mL acetonitrile and finally with 30 mL diethyl ether, and dried in a vacuum desiccator for 5 days. The yield was 1.40 g [96% of theory based on 1,1-dimethylhydrazine; mp 138-139°C with decomposition (lit 134°C)].

Anal. Calcd. for $[(CH_3)_2N(NH_2)_2]Cl$: C, 21.53; H, 9.03; N, 37.66. Found: C, 20.92; H, 8.95; N, 37.21.

About 86% of the crown ether was recovered by evaporation of the liquid obtained by combining the filtrate together with the diethyl ether and acetonitrile used for washing.

The infrared spectrum, Figure 3.1, of 2,2-dimethyltriazanium chloride is identical with that reported in the literature.[60]

The ^{1}H NMR spectrum of the compound is given in Figure 3.2. The peak at $\delta = 3.495$ refers to protons of the methyl groups, the peak at

Table 3.3

Nuclear Magnetic Resonance Data[a]

$[(CH_3)_2N(NH_2)_2]^+Cl^-$

	δ (ppm)	Assignment	Relative Area Ratio
^1H DMSO-d6	3.495 (s)	$-CH_3$	3
	6.673 (s)	$-NH_2$	2

	δ (ppm)	Assignment	J (Hz)
^{13}C DMSO-d6	59.550 (q)	CH_3	J_{CH} = 144.880

	δ (ppm)	Assignment	J (Hz)
^{15}N DMSO-d6	-274.721 (s)	$\overset{+}{N}(CH_3)_2$	-
	-245.784	NH_2	J_{NH} = 66.005

$[(CH_3CH_2)_3NNH_2]^+Cl^-$

	δ (ppm)	Assignment	Relative Area Ratio
^1H $CDCl_3$	1.42 (t)	CH_3	9
	3.69 (q)	CH_2	6
	6.58 (s)	NH_2	2

Table 3.3--continued

$(CH_3CH_2)_3N$

	δ (ppm)	Assignment	Relative Area Ratio
^1H	0.98 (t)	CH_3	3
$CDCl_3$	2.44 (q)	CH_2	2

a s, Singlet; d, doublet; t, triplet, q, quartet

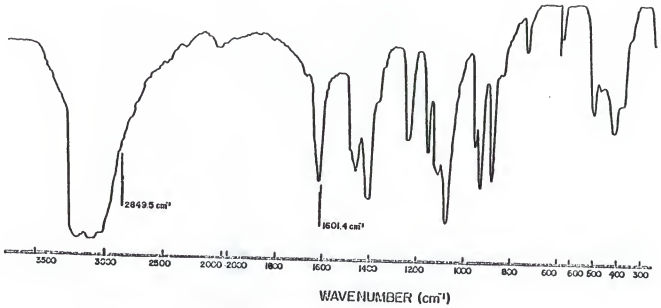


Figure 3.1. Infrared spectrum of 2,2-dimethyltriazanium chloride.

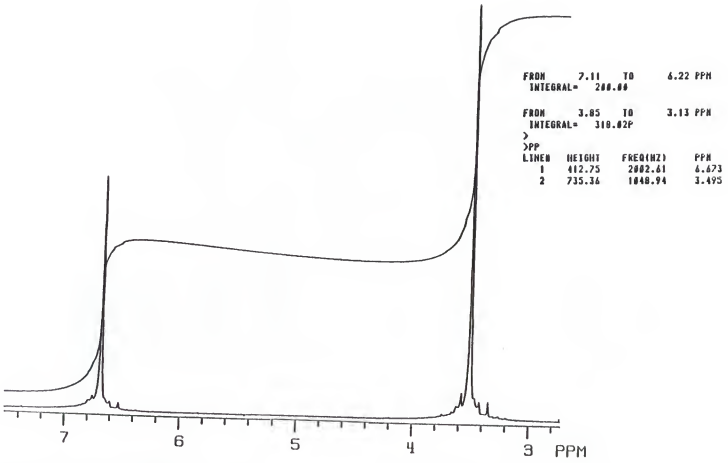


Figure 3.2. The 300 MHz ^{1}H NMR spectrum of 2,2-dimethyltriazanium chloride in DMSO-d6 solution.

δ = 6.673 to NH_2 protons. The ratio of the areas under the two peaks is 6:4, respectively.

The ^{13}C NMR spectrum, Figure 3.3 (a,b), consists of two peaks at δ = 39.500 and δ = 59.550 ppm. The peak at 39.500 is a heptet and is attributed to the solvent; the peak at 59.550 [J_{CH} = 144.880 Hz] is a quartet and is attributed to the methyl group of the compound. For $CH_3NR_3^+$, J_{CH} is reported by Abraham and Loftus to be 145 Hz.[95]

The ^{15}N NMR spectrum, Figure 3.4, shows two peaks: a singlet at δ = -274.721 ppm, and a triplet centered at δ = -245.784 ppm (J_{NH} = 66.005 Hz). The first peak is attributed to the quaternary nitrogen, and the second one is attributed to the NH_2 nitrogen.

The Interaction of 18-Crown-6 Ether with Chloramine

Into a 250 mL round-bottom flask containing a teflon coated magnetic stirring bar, and fitted with dropping funnel was placed 41 mL of a solution of chloramine in diethyl ether (0.14 M). A solution of 1.50 g (~5.7 mmol) of 18-crown-6 ether in 10 mL of diethyl ether was added dropwise over a period of 30 min. External cooling by means of an ice bath was maintained with stirring overnight. The white crystals which formed during the course of the reaction were removed by filtration, washed four times with 10 mL portions of diethyl ether, and dried by a flow of prepurified nitrogen. The solid was strongly oxidizing toward an acidified potassium iodide solution. Weight: 1.10 g (61% of theory); decomposed at 115°C.

Anal. Calcd. for 18-crown-6·NH_2Cl: C, 45.64; H, 8.29; N, 4.43; Cl, 11.26. Found: C, 44.27; H, 9.23; N, 4.23, Cl, 10.85.

The infrared spectrum of the isolated solid is given in Figure 3.5. In addition to those bands associated with the crown ether, the spectrum

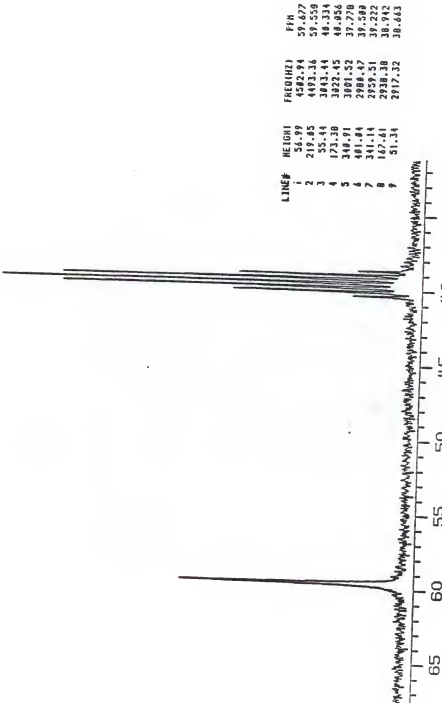


Figure 3.3. (a) Proton noise decoupled 300 MHz ^{13}C NMR spectrum of 2,2-dimethyltriazanium chloride in DMSO-d6 solution.

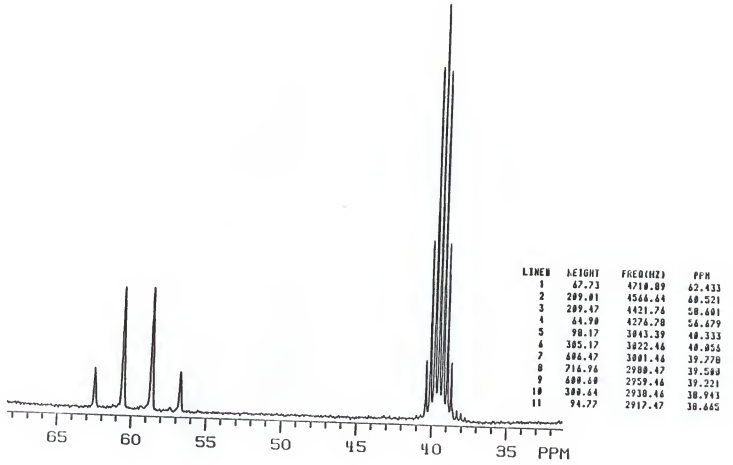


Figure 3.3 (continued). (b) The undecoupled ^{13}C NMR spectrum of 2,2-dimethyltriazanium chloride.

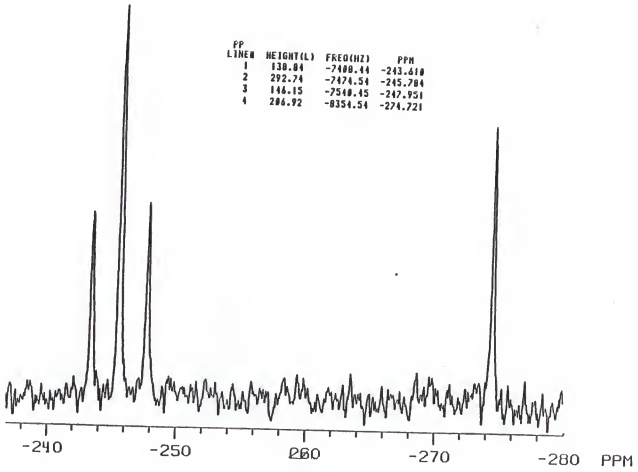


Figure 3.4. Proton noise undecoupled 300 MHz ^{15}N NMR spectrum of 2,2-dimethyltriazanium chloride in DMSO-d6 solution.

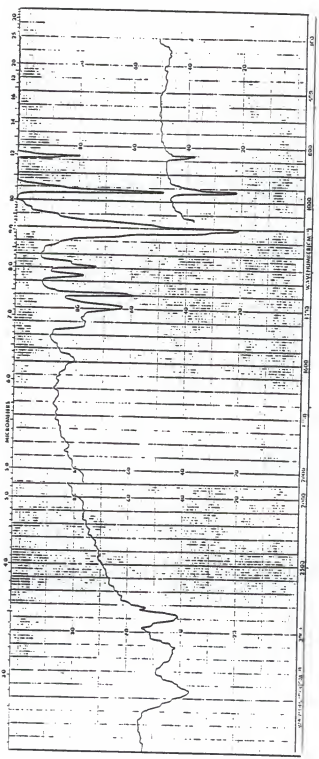


Figure 3.5. Infrared spectrum of 18-crown-6 ether, chloramine adduct.

shows two bands at 3320-3600 and 3040-3280 cm^{-1} which may be attributed to asymmetrical and symmetrical NH stretch, respectively, in chloramine.[114]

As a result of the low stability of the adduct in solutions of chloroform, other spectrometric measurements on the adduct were not very useful.

The Interaction of 18-Crown-6 Ether with Monomethylchloramine and Dimethylchloramine

To a stirred solution of about 16 mmol of 18-crown-6 ether in 30 mL of diethyl ether was added 20 mL of 1.65 M solution of monomethylchloramine in diethyl ether. After 18 hr in the freezer, long needle-like crystals were formed at the bottom of the reaction flask. The crystals could not be isolated because of their low stability at room temperature.

Flat, square-shaped crystals, of the same behavior as those in the case of monomethylchloramine, were obtained from the reaction of 18-crown-6 ether with dimethylchloramine in diethyl ether.

18-Crown-6 Ether-Chloramine Adduct as Aminating Reagent for Triethylamine

Two grams (6.33 mmol) of the 18-crown-6 ether-NH_2Cl dissolved in 150 mL diethyl ether was placed in a 250 mL flask with a magnetic stirring bar; then 0.80 mL (5.73 mmol) of triethylamine was added. The slow reaction was allowed to proceed for 3 days, at which time the reaction mixture was filtered off, washed with diethyl ether, and dried. The white solid was extracted with chloroform, and white needle-like crystals were precipitated from the chloroform by the addition of diethyl ether (mp 187-188°C; lit 177-178°C).[64]

Anal. Calcd. for $[(CH_3CH_2)_3NNH_2]Cl$: C, 47.20; H, 11.22; N, 18.35; Cl, 23.22. Found: C, 47.17; H, 10.75; N, 18.29; Cl, 23.58.

The infrared spectrum, Figure 3.6, of the solid product shows two strong bands at 990 and 920 cm^{-1} which are characteristic for quaternary ammonium compounds $[-N(R_3)^+]A^-$. It shows also two bands at 1620 and 875 cm^{-1} which are characteristics of $-NH_2$ group.

The ^1H NMR spectrum of the product is given in Figure 3.7. The spectrum showed five peaks. Peak A refers to the internal standard, peak B to CH_3, peak C to CH_2, peak D to NH_2, and peak E to undeuterated impurity in chloroform. The peaks B, C and D correspond to values of 1.42, 3.69 and 6.58 ppm, respectively. The ratio of the areas under peaks B, C and D is 9:6:2. Figure 3.8 shows, for comparison, the ^1H NMR spectrum of triethylamine.

Discussion and Conclusions

The reaction of a solution of chloramine in diethyl ether with a solution of 1,1-dimethylhydrazine and a catalytic amount of 18-crown-6 ether in diethyl ether resulted in the formation of 2,2-dimethyltrazanium chloride in high yield and high purity according to Equation 10.

$$(CH_3)_2NNH_2 + NH_2Cl \xrightarrow[\text{ether}]{\text{18-crown-6}} [(CH_3)_2N(NH_2)]^+Cl^- \qquad (10)$$

The infrared spectrum of the product is given in Figure 3.1, and the data are summarized in Table 3.2. The spectrum shows a strong absorption at 930 cm^{-1} which is associated with quaternary ammonium compounds (lit 900-980 cm^{-1}). The spectrum shows also two strong absorptions at 1620 and 860 cm^{-1} which are assigned for $-NH_2$ group (lit 1590-1650 and 850 cm^{-1}, respectively). Further proof of the identity of the product is

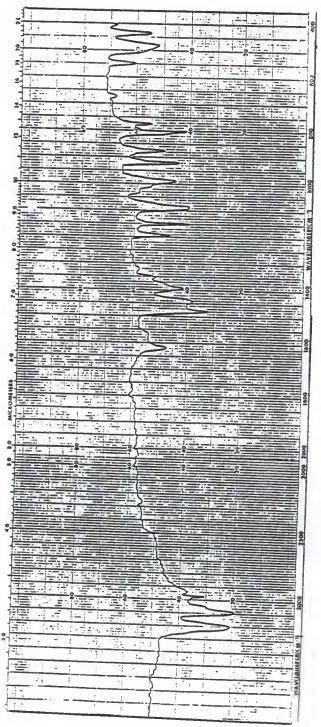


Figure 3.6. Infrared spectrum of 1,1,1-triethylhydrazinium chloride.

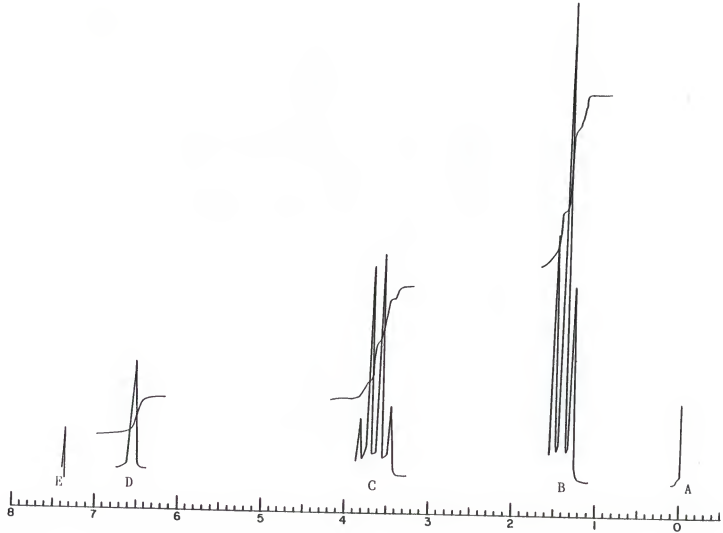


Figure 3.7. The 60 MHz ^{1}H NMR spectrum of 1,1,1-triethylhydrazinium chloride in $CDCl_3$ solution.

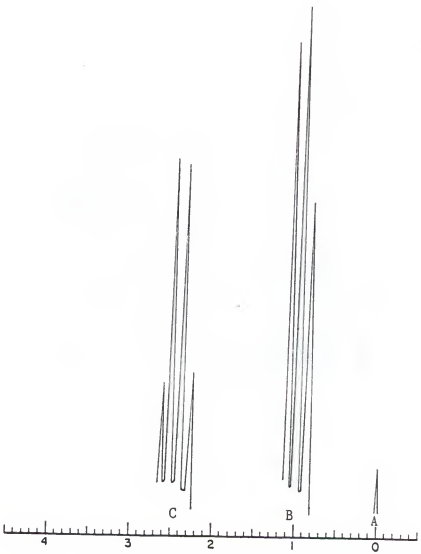
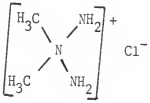


Figure 3.8. The 60 MHz ^{1}H NMR spectrum of triethylamine in $CDCl_3$ solution.

provided by the nuclear magnetic resonance spectrum. A summary of the NMR data is reported in Table 3.3. The ^{1}H NMR spectrum (Figure 3.2) shows two peaks: a singlet at δ 3.495 and is assigned to the six protons of the two methyl groups, the other peak at δ 6.673 is another singlet but of lower intensity and refers to the four protons of the two amino groups. The ratio of the areas under the two peaks is consistent with our assignment and is about 3:2, respectively. Figure 3.3 (a,b) shows the ^{13}C NMR spectrum of the product. As one might expect, the spectrum shows only one peak for the product, and it is a quartet centered at δ 59.550. The carbon-proton coupling constant J_{CH} is 144.88 Hz, and it is in agreement with the J_{CH} reported in Chapter 2 for the α-carbon of 2,2-diallyltriazanium chloride. The ^{15}N NMR spectrum (Figure 3.4) shows two different types of nitrogen atoms in the product as indicated by the presence of two peaks. The first peak δ -274.721 is a singlet, and it must be for the quaternary nitrogen. The second peak at higher field is a triplet centered at δ -245.784, and it refers to the $-NH_2$ nitrogens. The nitrogen-hydrogen coupling constant J_{NH} is about 66.0 Hz, and it is consistent with the value found for J_{NH} in 2,2-dimethyltriazanium chloride reported in Chapter 2.

The previous analysis shows that our experimental data are consistent with and in support of the structural formula for 2,2-dimethyltriazanium chloride as reported in previous studies.[65] The structure of the cation was described to consist of a central nitrogen surrounded tetrahedrally by two amino and two methyl groups.



To illustrate the effect of 18-crown-6 ether on the production of 2,2-dimethyltriazanium chloride, Equations 11, 12 and 13 represent the chloramination of 1,1-dimethylhydrazine by chloramine in ether in the absence of 18-crown-6 ether.[62,63]

$$\underset{30\ \text{mmol}}{(CH_3)_2NNH_2} + \underset{30\ \text{mmol}}{NH_2Cl} \xrightarrow[4\ \text{hr}]{\text{ether, } 0°C} \underset{4.9\ \text{mmol}}{[(CH_3)_2N(NH_2)_2]^+Cl^-} + \ldots \qquad (11)$$

$$\underset{33\ \text{mmol}}{(CH_3)_2NNH_2} + \underset{100\ \text{mmol}}{NH_2Cl} \xrightarrow[0°C,\ 25\ \text{hr}]{\text{ether, } NH_3} \underset{14\ \text{mmol}}{[(CH_3)_2N(NH_2)_2]^+Cl^-} + \ldots \qquad (12)$$

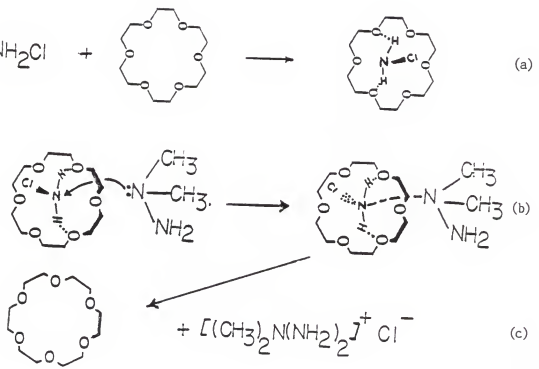
$$\underset{26.3\ \text{mmol}}{(CH_3)_2NNH_2} + \underset{25.2\ \text{mmol}}{NH_2Cl} \xrightarrow[1\ \text{hr}]{\text{ether, } 20°C} \underset{0.15\ \text{mmol}}{[(CH_3)_2N(NH_2)_2]^+Cl^-} + \ldots \qquad (13)$$

The yield of 2,2-dimethyltriazanium chloride in the above reactions in ether ranges from 0.6 to 42%. Equation 14 represents the same reaction under the same condition but in the presence of 18-crown-6 ether and indicates almost quantitative yield.

$$\underset{13.0\ \text{mmol}}{(CH_3)_2NNH_2} + \underset{13.3\ \text{mmol}}{NH_2Cl} \xrightarrow[18\text{-crown-6}]{\text{ether, } 0°C} \underset{12.4\ \text{mmol}}{[(CH_3)_2N(NH_2)_2]^+Cl^-} \qquad (14)$$

There have been several reports of nucleophilic substitution reaction S_N2 in the presence of crown ethers where similar results were obtained; however, no mechanisms have been offered. The mechanism of the action of 18-crown-6 ether on the chloramination of 1,1-dimethylhydrazine by chloramine is uncertain and needs more study. However, we suggest an S_N2 type mechanism in which the first step might be the formation of an adduct or a complex between chloramine and the crown ether--as we will see later in the chapter--through the formation of hydrogen bonds between

the two hydrogens of the chloramine molecule (NH_2Cl) and the oxygen atoms of the crown ether. Since the six oxygen atoms of the crown ether are in one plane forming a ring, the chloramine has to be above or below the plane of the ring with the chlorine atom pointing up or down, respectively. The formation of such an adduct enhances the reaction to form 2,2-dimethyltriazanium chloride as follows: The structure of the adduct as described above makes the electron deficient nitrogen in the chloramine molecule more susceptible to attack by a nucleophile like 1,1-dimethylhydrazine which presumably will attack from the direction opposite to the chlorine atom (leaving group) and where the steric hindrance is minimal. This can be represented as the following:



The last step (c) is enhanced by the breaking of the polar Cl-N bond and the formation of the new N-N bond; both these factors increase the

electron density on the chloramine nitrogen which causes its hydrogens to become less positive and therefore less capable of participating in hydrogen bonds. Step c is enhanced also by the increase in steric hindrance in the transition state due to the attachment of 1,1-dimethylhydrazine.

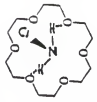
An alternative explanation might be that the formation of the adduct (step a) inhibits some side reactions which are known to lower the yield of 2,2-dimethyltriazanium chloride and which involve the initial formation of dialkyldiazine by the abstraction of hydrogen atom(s) from the amino nitrogen in 1,1-dimethylhydrazine.

Another object of this study was to determine if the 18-crown-6 ether forms a stable adduct with chloramine. Our study shows that an etheral solution of 18-crown-6 ether reacts with a solution of chloramine in ether to form a stable adduct which is strongly oxidizing toward an acidified potassium iodide solution.

The elemental analysis of the adduct shows that the adduct contains one mole of chloramine per mole of the crown ether. The infrared spectrum is shown in Figure 3.5, and the data are summarized in Table 3.2. The spectrum shows the bands associated with 18-crown-6 ether as well as two absorptions in the regions 3320-3600 and 3040-3280 cm^{-1} which were described for chloramine as asymmetric and symmetric NH stretches, respectively.

The structure of the adduct of the crown ether with chloramine is uncertain and more work, probably x-ray analysis will be required to determine the exact nature of this adduct. However, it has been reported that thiourea and related compounds form complexes with crown ethers,[115] and several possibilities for their structures have been discussed; e.g., the complexes might be inclusion compounds or they might be crystals with

the guest molecules present as inerstitial components. The relatively high melting point and the fixed composition of the chloramine-18-crown-6 ether adduct do not agree with the above assumptions. Instead, a better description might be that hydrogen bonds between the oxygen atoms of 18-crown-6 ether and the two hydrogen atoms of the chloramine molecule take part in the complexation with chloramine molecule as shown below.



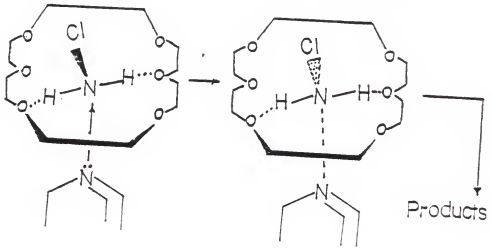
This description would explain the low stability of the adduct of 18-crown-6 ether with monomethylchloramine (CH_3)NHCl which has only one hydrogen atom on the nitrogen atom, and the even lower stability of the 18-crown-6 ether adduct with dimethylchloramine which has no hydrogen atoms on the nitrogen atom.

The third purpose of this study was to determine the action of the chloramine-18-crown-6 ether adduct as a chloramination agent toward nucleophiles. This was done by running a reaction between the chloramine adduct and triethylamine as a nucleophile, using diethyl ether as a solvent. The reaction resulted in the formation of a white solid melting at 187-188°C ($[(CH_3CH_2)_3NNH_2]^+Cl^-$; lit mp 177-178°C). The infrared spectrum (Figure 3.6) shows two absorptions at 990 and 920 cm^{-1} which are characteristic absorptions for quaternary ammonium compounds. The spectrum shows also the two absorptions associated with the $-NH_2$ group at 1620 and 875 cm^{-1}.

The ^1H NMR spectrum is shown in Figure 3.7, and the data are summarized in Table 3.2. The spectrum shows five peaks, A-D: The peaks A and B are due to the internal reference TMS and the solvent $CDCl_3$,

respectively. Peak B is a triplet centered at δ 1.42 and is assigned to the methyl protons. Peak C is a quartet centered at δ 3.69 and is assigned for the methylene protons. Peak D is a singlet δ 6.58 and assigned to the amino protons; this assignment is consistent with our earlier ones to the amino protons in 2,2-dimethyl- and 2,2-diallyltriazanium chlorides. Comparison of the ^1H NMR spectra of 1,1,1-triethylhydrazinium chloride and triethylamine (Figures 3.7 and 3.8, respectively) shows that peaks corresponding to the $-CH_2$ and $-CH_3$ protons are shifted toward lower field by 1.25 and 0.44 ppm, respectively, which is to be expected in terms of the inductive effect of the quaternized nitrogen atom in the compound.

The experimental results show that the compound obtained from the reaction of the chloramine-18-crown-6 ether adduct with triethylamine is 1,1,1-triethylhydrazinium chloride. To explain its formation, a mechanism similar to the one proposed earlier for the action of 18-crown-6 ether on the chloramination of 1,1-dimethylhydrazine is shown below.



The fact that the reaction was slower than in the case of 1,1-dimethylhydrazine might be explained in terms of the steric effect of the three ethyl groups in triethylamine.

Summary

It has been shown in this study that when the reaction of chloramine with 1,1-dimethylhydrazine is carried out in the presence of a catalytic amount of 18-crown-6 ether, both the yield and purity of 2,2-dimethyltriazanium chloride are improved. This was proven by elemental analysis, infrared, and nuclear magnetic resonance studies. The ^{13}C and ^{15}N NMR spectra of 2,2-dimethyltriazanium chloride are reported for the first time and they are consistent with what is found for 2,2-diallyltriazanium chloride.

An S_N2-type mechanism which might explain the action of 18-crown-6 ether on the chloramination of 1,1-dimethylhydrazine to produce 2,2-dimethyltriazanium chloride is postulated. The first step in this mechanism is the formation of an adduct or a complex between chloramine molecule and the crown ether. This step is followed by another step in which 1,1-dimethylhydrazine attacks the complex from the direction opposite to that of the chlorine atom, where steric hindrance is minimal, leading to the formation of 2,2-dimethyltriazanium chloride through a transition state in which the H_2N-Cl bond starts to break and the H_2N-$N(NH_2)(CH_3)_2$ bond starts to form.

The interaction between 18-crown-6 ether and a chloramine solution in diethyl ether results in the formation of an adduct between the crown ether and chloramine as was shown by the elemental analysis of the product and indicated by the infrared spectrum. The structure of the adduct

is assumed to involve hydrogen bonds between the two hydrogen atoms of chloramine molecule and the planar oxygen atoms of the crown ether. Furthermore, the chloramine-18-crown-6 ether adduct was found to act as a chloramination agent toward triethylamine according to Equation 15.

$$(C_2H_5)_3N + \text{18-crown-6}\cdot NH_2Cl \longrightarrow [(C_2H_5)NNH_2]^+Cl^- + \text{18-crown-6} \quad (15)$$

The product was identified by its IR and ^1H NMR spectra. The proposed mechanism is similar to the one proposed earlier to the action of 18-crown-6 ether on 1,1-dimethylhydrazine.

CHAPTER FOUR

A STUDY OF THE COMPLEXES OF SOME CROWN ETHERS WITH ACETONITRILE

Introduction

Approximately a quarter century ago, Pedersen at the duPont Company identified a macrocyclic polyether as an unexpected by-product and discovered that it had the unusual property of complexing with alkali and alkaline-earth metal cations. He subsequently synthesized a series of "crown ethers," as he called them, and in 1967 reported them and some of their characteristics.[116,117] The discovery of crown compounds aroused a great deal of interest in a variety of different fields.

Since their discovery, the chemistry and applications of the crown ethers has grown rapidly and with remarkable results. Several hundreds of crown ethers and their analogues, including aza- and thia-crown compounds, have been synthesized, and their specific properties have been investigated.

A large number of complexes between crown ethers and cations--not only of the Group I and II metals, but also some transition metals. There have also been reports of many complexes of crown ethers with polar organic compounds, such as nitro compounds.

It has been reported that acetonitrile, as a polar organic compound, forms a complex with the 18-crown-6 ether, and this can be utilized for the purification of 18-crown-6.[118,119] It was also mentioned that this complex is unstable in air as it loses acetonitrile

rapidly.[118] However, characterization of this complex of the 18-crown-6 ether was not published. Further, it was thought that the complex formation of acetonitrile with 18-crown-6 could be extended to other crown ethers having the same cavity size as that of 18-crown-6.

There are five possible stereoisomers of dicyclohexyl-18-crown-6 ether because of cis and trans isomerism of the four bridgeheads on the cyclohexyl rings as shown in Figure 4.1; however, the product of hydrogenation of dibenzo-18-crown-6 ether is a mixture of isomer A and isomer B.[120] The two isomers, A and B, were separated by elution chromatography using an alumina column and ether/hexane eluate.[121] Izatt et al.[122] isolated isomers A and B utilizing the difference in solubilities of the Pb(II) and H_3^+O complexes of each isomer in water. Both separations are expensive and time consuming, and low yields are obtained.

Burden et al.[123] reported that the stability constant values of the complexes of the two isomers, A and B, of dicyclohexyl-18-crown-6 with NaCl, KCl and CsCl followed the order of cis-syn-cis(A) > cis-anti-cis(B).

It was further thought that there was a possibility that the interaction of acetonitrile with a mixture of isomers A and B of dicyclohexyl-18-crown-6 ether might provide a pathway to the isolation of the isomers (cis-syn-cis and cis-anti-cis).

Therefore, we decided to study, using IR, ^1H NMR and ^{13}C NMR, (1) the complex formation of acetonitrile with 18-crown-6 ether; (2) to synthesize similar complexes of acetonitrile with some other crown ethers; and (3) to investigate the utility of acetonitrile with respect to the purification and separation of a mixture of isomers of dicyclohexyl-18-crown-6 ether.

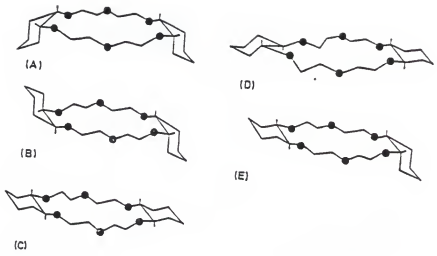


Figure 4.1. The five thecretical isomers available for dicyclohexyl-18-crown-6 ether. Isomers A and B are the only two so far isolated. A, Isomer A, cis-syn-cis (meso); B, Isomer B, cis-anti-cis (dl); C, trans-syn-trans (meso; D, trans-anti-trans (dl); E, trans-anti-cis (dl).

Historical Background

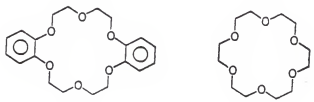
Classification and Nomenclature of Crown Compounds

Crown compounds are generally described as "macrocyclic compounds" having hetero atoms such as O, N or S as the electron donor atoms in their ring structures and the property of incorporating cations into their cavities. Multicyclic compounds consisting of two or more rings are also crown compounds. In a broad sense, crown compounds are "multidentate macrocyclic compounds" or "macroheterocycles."

The macrocyclic polyethers having only O atoms as the donor atoms are termed crown ethers. Cyclic amino ethers in which N substitutes for some of the O donor atoms of a crown ether are known as azacrown ethers, and cyclic polyether sulfides in which S substitutes for some of the O donors are called thiacrown ethers. Cyclic compounds with 3 kinds of donor atoms, O, N and S are called azathiacrown ethers. Macrocyclic polyamines having only N atoms as donors are called azacrowns, and macrocyclic polysulfides having only S atoms as donors are termed thiacrowns.

Because their formal names, following IUPAC nomenclature rules, are quite long and complicated, Pedersen proposed convenient, brief names for the nomenclature of the crown ethers. His general rules for nomenclature are as follows: for crown ethers having a hydrocarbon ring, the names consist of (1) the kind and number of the group substituted in the polyether ring, (2) the total number of atoms which constitute the crown ring (corresponding to the cavity size), (3) the class name "crown," and (4) the number of O donor atoms, that is, the ether linkage in the crown ring, combined with hyphens such as "dibenzo-18-crown-6" (Figure 4.2a). For crown ethers without any substituted group, the crown names consist

of [the total number of atoms which constitute the crown ring]-["crown"]-[number of O donor atoms], such as "18-crown-6" (Figure 4.2b).



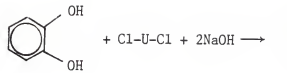
a b

Figure 4.2. Dibenzo-18-crown-6 (a) and 18-crown-6 (b).

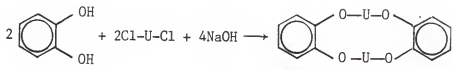
Synthesis and Properties of Crown Ethers[124]

There is a great variety of synthetic methods for crown ethers, but the most important aspect of any synthesis is to minimize the side reaction that may produce linear polymers in order to obtain the cyclic compound preferentially from the cyclization reaction. To depress the formation of by-products, the following methods are employed: (1) a high dilution method, to encourage ring closure which is an intramolecular reaction; (2) two-step condensation, condensation of one of the terminal groups on both bifunctional compounds and separation of the reaction product followed by a ring closure reaction; and (3) a template reaction using a metal ion whose ionic diameter corresponds to the cavity size of the desired crown ring.

The general method for the preparation of aromatic crown ethers is the Williamson condensation reaction exemplified by stoichiometric Equations 16-18.

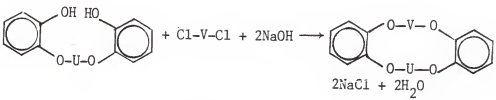


(16)



(17)

+ 4NaCl + 4H_2O



(18)

In general, U and V represent divalent organic groups, $\leftarrow CH_2CH_2\rightarrow_n CH_2CH_2-$ ($n \geq 1$).

Alicyclic crown ethers are commonly prepared by hydrogenation of the corresponding aromatic crown ethers.[124]

Generally speaking, aromatic crown ethers are only slightly soluble in water, alcohols, and conventional solvents at room temperature, but the are soluble in solvents like methylene chloride, chloroform, pyridine, and formic acid. Alicyclic crown ethers are more soluble than the corresponding aromatic crown ethers. They are soluble in organic polar solvents and also in low or nonpolar solvents such as aromatic and aliphatic hydrocarbons.

Characteristics of Crown Ethers[125-132]

The most striking characteristic of crown compounds is their ability to form stable complexes. During complexation, the cation portion of a metal salt or an organic ionic compound is bound by a crown compound bearing donor atoms such as O, N and S. The formation of these

complexes was detected qualitatively by measuring (1) solubility changes of the crown ethers and salt in various solvents, and (2) characteristic changes in the UV spectra of the aromatic crown ethers.

The complexation ability of a crown ether and the stability of the resulting complexes depend on the relative diameter of the cavity in the crown ether and the diameter of the cation; they are also influenced by the charge of O atoms present in the crown ether. The ion-selective complexation ability of crown ethers is a product of these characteristics. Furthermore, such complexes become soluble in various organic solvents, including nonpolar solvents, because crown compounds have hydrophobic groups.

Pedersen listed the following factors that affect the stability of the formed complex:

(1) The relative sizes of the ion and the cavity of the crown ether: The more closely they match, the more stable is the complex formed.

(2) The number of O donor atoms in the ring: Stability of the complex increases as the number of O donors increases.

(3) The coplanarity of O donor atoms: The more O donors are arranged on a plane, the more stable is the complex formed.

(4) The symmetry of the arrangement of O donor atoms: The more O donors are arranged symmetrically, the more stable is the complex formed.

(5) The basicity of O donor atoms: Stability of the complex increases with increasing basicity. The basicity of an O atom bonded to an aliphatic carbon atom is greater than that of an O atom bonded to an aromatic ring.

(6) Steric hindrance in the polyether ring: The less steric hindrance there is, the more stable is the complex formed.

(7) The solvent and extent of solvation of the ion and the binding sites: The less solvation, the more stable is the complex formed.

(8) The electric charge on the ion: The influence of the ionic charge has not been determined experimentally.

Experimental

Materials

The crown ethers used in this work were obtained from the Aldrich Chemical Co. They were dried under high vacuum for 24 hr and used without any further purification. Acetonitrile (Eastman Kodak, ACS reagent) was dried by distillation over P_4O_{10} and then stored over molecular sieves.

Analyses

Elemental analyses were done by Galbraith Laboratories Inc., Knoxville, Tennessee. Melting points were obtained in sealed capillary tubes in a Thomas-Hoover capillary melting point apparatus and are reported uncorrected.

Infrared Spectra

Infrared spectra were recorded on a Perkin-Elmer 283B infrared spectrophotometer using sodium chloride optics. The spectra of the solids were obtained from Nujol mulls. A summary of the infrared data is found in Table 4.1.

Nuclear Magnetic Resonance Spectra

The ^1H NMR spectra were determined using a Varian EM 360L NMR spectrometer and/or NT 300 Nicolet spectrometer. The ^{13}C NMR spectra were obtained using NT 300 Nicolet spectrometer. The spectra were determined using deuterated chloroform as the solvent and tetramethylsilane as the internal standard. The ^1H and ^{13}C chemical shift values are listed in Table 4.2.

Table 4.1

Infrared Absorption in cm^{-1} [a]

18-crown-6 ether•$2CH_3CN$ $C_{12}H_{24}O_6 \cdot 2CH_3CN$ (Nujol)	3455 (m,b), 3390 (sh,w), 2900 (vs), 2235 (w), 1450 (vs), 1375 (vs), 1340 (sh,m), 1275 (vw), 1245 (vw), 1135 (sh,m), 1100 (vs), 960 (m), 830 (m), 715 (m)
Dicyclohexyl-18-crown-6 ether•$2CH_3CN$ (Nujol)	3380 (w), 3460 (sh, vw), 2900 (vs), 2270 (vw), 2240 (m), 1450 (vs), 1400 (vw), 1360 (s), 1335 (m), 1290 (m), 1245 (s), 1230 (vw), 1195 (m), 1100 (vw), 990 (s), 950 (w), 930 (s), 910 (vw), 880 (w), 840 (s), 810 (s), 800 (vw), 715 (w), 660 (m), 600 (m)
Dicyclohexyl-18-crown-6 ether mp 68-69°C (Nujol)	2900 (vs), 1455 (vs,d), 1375 (s), 1365 (sh,s), 1305 (vw,d), 1100 (s), 990 (vw), 975 (vw), 935 (vw), 840 (vw), 720 (s)
Dibenzo-18-crown-6 ether (Nujol)	2950 (vs), 1590 (m), 1510 (w), 1460 (vs), 1375 (vs), 1365 (sh,s), 1260 (m), 1230 (m), 1130 (s), 995 (w), 930 (m), 775 (vw), 750 (sh,w), 740 (m), 725 (m,d), 595 (w)

a b, Broad; d, doublet; m, medium; s, strong; sh, shoulder; v, very; w, weak

Table 4.2

Nuclear Magnetic Resonance Data

	^1H	
Compound	δ (ppm)[a]	Assignments
18-crown-6 ether	3.71 (s)	CH_2-O
18-crown-6 ether·$2CH_3CN$	2.05 (s)	CH_3-CN
	3.80 (s)	CH_2-O
Dicyclohexyl-18-crown-6 ether	0.80-2.10	-CH_2-(cyclohexyl)
	3.30-4.00	-CH_2-O and the four bridgeheads on the cyclohexyl ring
Dicyclohexyl-18-crown-6 ether·$2CH_3CN$	1.10-1.90	-CH_2-(cyclohexyl ring)
	2.01	CH_3-CN
	3.40-3.90	CH_2-O and the four bridgeheads on the cyclohexyl ring

a s, Singlet; d, doublet; t, triplet; q, quartet

Table 4.2--continued

^1H Relative Area Ratio		^{13}C	
Found	Theory	δ (ppm)[a]	Assignments
		70.235 (s)	CH_2-O
1	1	1.570 (q)	$\underline{CH}_3$-CN
4	4	70.361 (t)	CH_2-O
		77.000 (t)	solvent
		116.341 (s)	C≡N
1	1		
1.19	1.25	See Figure 4.11	
2.5	2.66	0.00 (q)	TMS
1.0	1.0	1.805 (q)	$\underline{CH}_3$-CN
3.0	3.33	21.984 (t)	CH_2-(cyclohexyl ring)
		27.538 (t)	CH_2-(cyclohexyl ring)
		67.807 (t)	CH bridgeheads
		70.463 (t)	CH_2-O
		75.567-78.590 (m)	solvent +?
		116.261 (s)	C≡N

The Interaction of 18-Crown-6 Ether with Acetonitrile

In a typical experiment, 0.25 mL of dry acetonitrile was added to a 5.0 g (0.0189 mol) sample of 18-crown 6 ether (mp 39-40°C) placed in a 100 mL round-bottom flask containing a teflon coated magnetic stirring bar. The mixture was stirred vigorously with gentle heating (30°C) until all the solid dissolved. The flask was finally put in the refrigerator (0°C) for 24 hr. The white crystals of the 18-crown-6 ether-acetonitrile complex were collected by filtration. The solid was dried by a continuous flow of dry nitrogen at room temperature for 5 hr. The product (5.9 g) melted at 79-80°C, and the yield based on 18-crown-6 ether was 90%.

Anal. Calcd. for 18-crown-6 ether·$2CH_3CN$: C, 55.47; H, 8.72; N, 8.08; O, 27.71. Found: C, 55.39; H, 8.22; N, 7.63; O, 28.76.

The infrared spectrum (Figure 4.3) of the product shows a broad peak at 3455 cm^{-1} which is associated with hydrogen bonds.[133] It also shows a weak peak at 2235 cm^{-1} characteristic of the C≡N bond. Aliphatic nitriles show this peak at 2240-2260 cm^{-1}.[134]

The proton nuclear magnetic resonance spectrum of this compound is found in Figure 4.4. This spectrum is composed of two singlets, A and B, which are attributed to the protons of the methyl group of acetonitrile[135] and the methylene protons of the crown ether, respectively. The area ratio of the two groups of protons is 1:4, as would be expected.

The ^{13}C NMR spectrum (Figure 4.5) shows four peaks at 1.570, 70.361, 77.00 and 116.341 ppm, which may be assigned to $\underline{C}H_3$-CN, $\underline{C}H_2$-O, solvent, and $\underline{C}\equiv N$, respectively.[95] Figure 4.6 shows, for comparison, the ^{13}C NMR spectrum of 18-crown-6 ether.

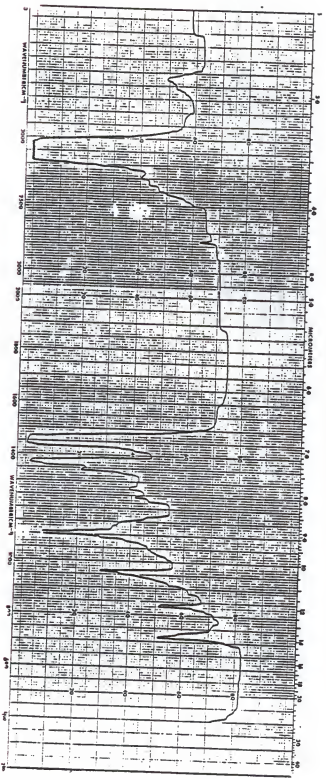


Figure 4.3. Infrared spectrum of 18-crown-6 ether, acetonitrile adduct.

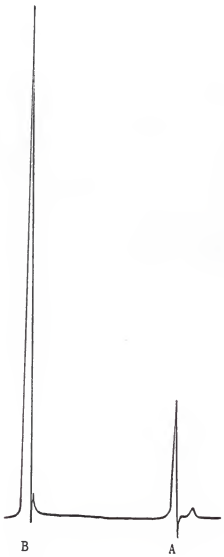


Figure 4.4. The 60 MHz ^{1}H NMR spectrum of 18-crown-6 ether, acetonitrile adduct in $CDCl_3$ solution.

Figure 4.5. Proton noise undecoupled 300 MHz ^{13}C NMR spectrum of 18-crown-6 ether, acetonitrile adduct in $CDCl_3$ solution.

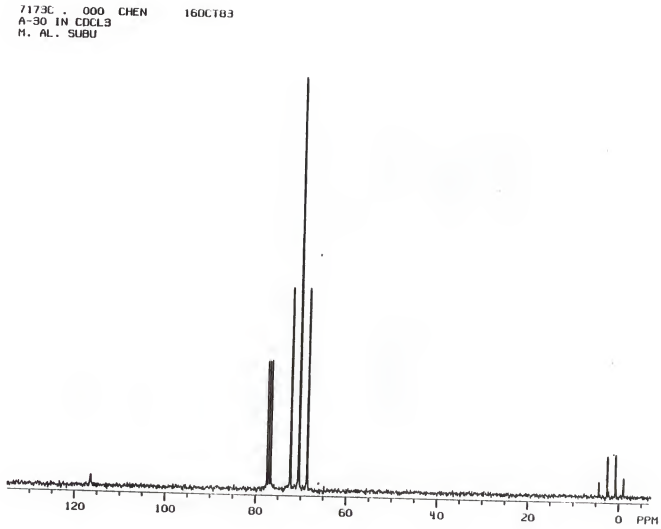
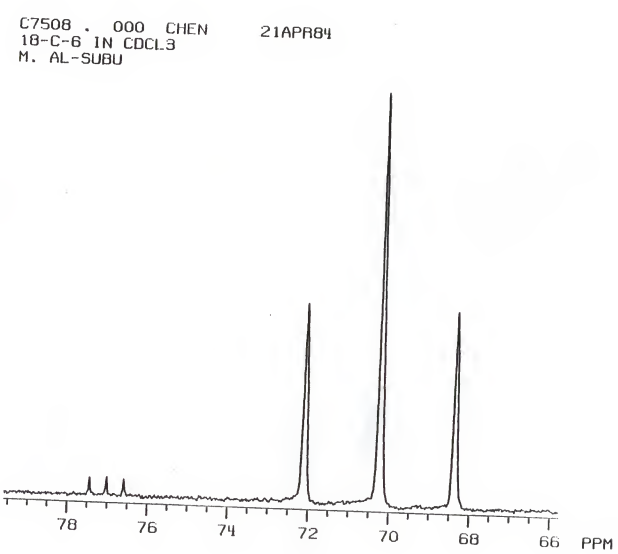

7173C . 000 CHEN 16OCT83
A-30 IN CDCL3
M. AL. SUBU
120
100
80
60
40
20
0
PPM

Figure 4.6. Proton noise undecoupled 300 MHz ^{13}C NMR spectrum of 18-crown-6 ether in $CDCl_3$ solution.


C7508 . 000 CHEN 21APR84
18-C-6 IN CDCL3
M. AL-SUBU
78
76
74
72
70
68
66
PPM

The Interaction of Dicyclohexyl-18-crown-6 Ether with Acetonitrile

A 1.0 g portion of the mixture of dicyclohexyl-18-crown-6 ether isomers (mp 36-56°C) was added to 15 mL of dry acetonitrile in a 50 mL round-bottom flask containing a teflon coated magnetic stirring bar. After the cyclic ether dissolved, the solution was kept in the refrigerator (0°C) for 6 days. The resulting white crystals were filtered, washed with diethyl ether, and dried under pre-purified nitrogen atmosphere (weight 0.41 g; mp 68-69°C).

Anal. Calcd. for dicyclohexyl-18-crown-6 ether•$2CH_3CN$: C, 63.41; H, 9.31; N, 6.16; O, 21.11. Found: C, 64.35; H, 9.67; N, 5.54; O, 20.44.

The acetonitrile was removed from the filtrate under vacuum, and the solid obtained was recrystallized from diethyl ether (dried over sodium metal) to yield 0.45 g of colorless crystals of IA (mp 59-60°C).

The acetonitrile was removed from the adduct dicyclohexyl-18-crown-6 ether•$2CH_3CN$ under high vacuum over 8 days. The residual dicyclohexyl-18-crown-6 ether (IB) melted at 68-69°C.

The infrared spectrum (Figure 4.7) of the adduct clearly shows the hydrogen bonds absorption centered at 3380 cm^{-1}. The peak associated with the C≡N bond is shown at 2240 cm^{-1}.

The ^1H NMR spectrum of the adduct (Figure 4.8) is in accord with the formula. It consists of three peaks assigned as follows: A, the methylene protons of the cyclohexyl rings; B, the methyl protons of acetonitrile; and C, the methylene protons of the crown ether together with the four bridgeheads protons. The area ratios are 2.5:1.0:3.0, respectively. For comparison, Figure 4.9 shows the ^1H NMR spectrum of dicyclohexyl-18-crown-6 ether.

The ^{13}C NMR spectrum (Figure 4.10) shows the two peaks characteristic of acetonitrile, together with those expected for the crown ether.

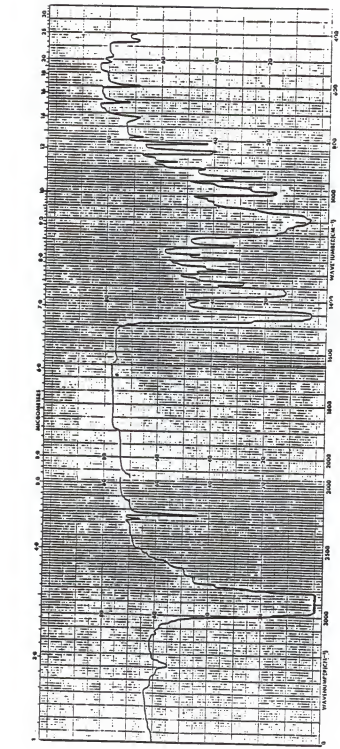


Figure 4.7. Infrared spectrum of dicyclohexyl-18-crown-6 ether, acetonitrile adduct.

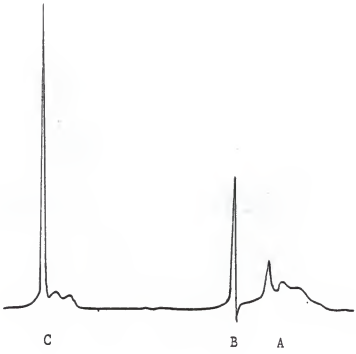


Figure 4.8. The 60 MHz ^{1}H NMR spectrum of dicyclohexyl-18-crown-6 ether, acetonitrile adduct in $CDCl_3$ solution.

Figure 4.9. The 300 MHz ^{1}H NMR spectrum of dicyclohexyl-18-crown-6 ether in $CDCl_3$ solution.

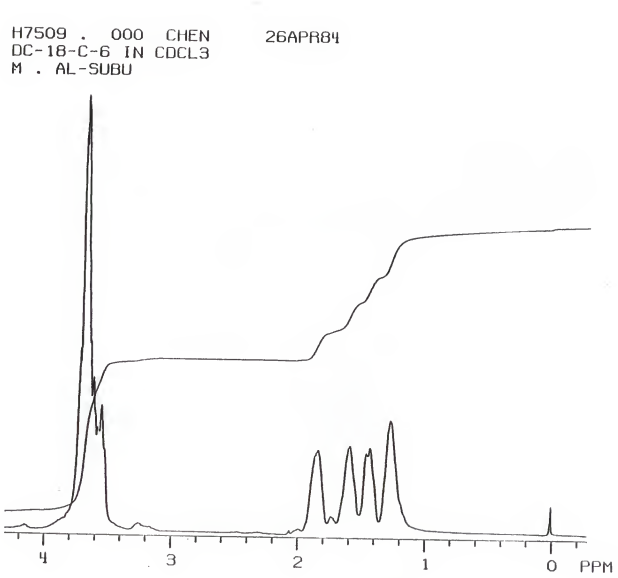
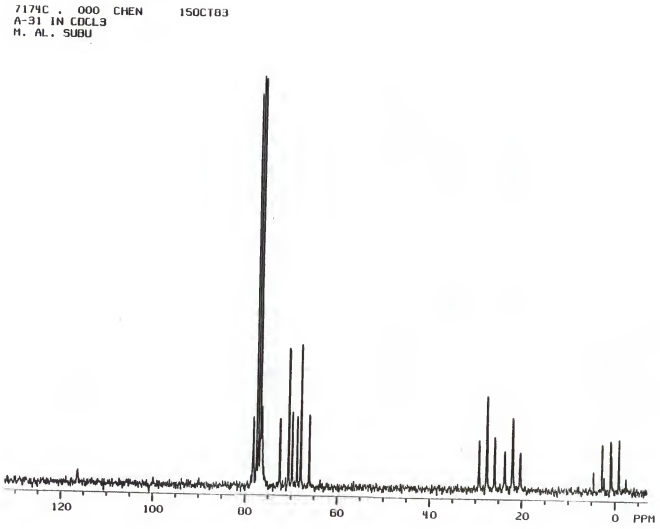

H7509 . 000 CHEN 26APR84
DC-18-C-6 IN CDCL3
M . AL-SUBU
4
3
2
1
0 PPM

Figure 4.10. Proton noise undecoupled 300 MHz ^{13}C NMR spectrum of dicyclohexyl-18-crown-6 ether, acetonitrile adduct in $CDCl_3$ solution.


7174C . 000 CHEN 15OCT83
A-31 IN CDCL3
M. AL. SUBU
120
100
80
60
40
20
0
PPM

This spectrum is interesting because it is simpler than that of the starting crown ether (Figure 4.11).

The infrared spectrum of the acetonitrile-freed dicyclohexyl-18-crown-6 ether (IB) is shown in Figure 4.12, and it is in agreement with that given by Pederson.[117] The ^{1}H NMR spectrum is found in Figure 4.13. It consists of two peaks, A and B. Peak A, 0.80-2.10 ppm, arises from the methylene protons of the cyclohexyl ring. Peak B, 3.30-4.0 ppm, arises from the methylene protons of the crown ether and the four bridgehead protons.

The Interaction of Dibenzo-18-crown-6 Ether with Acetonitrile

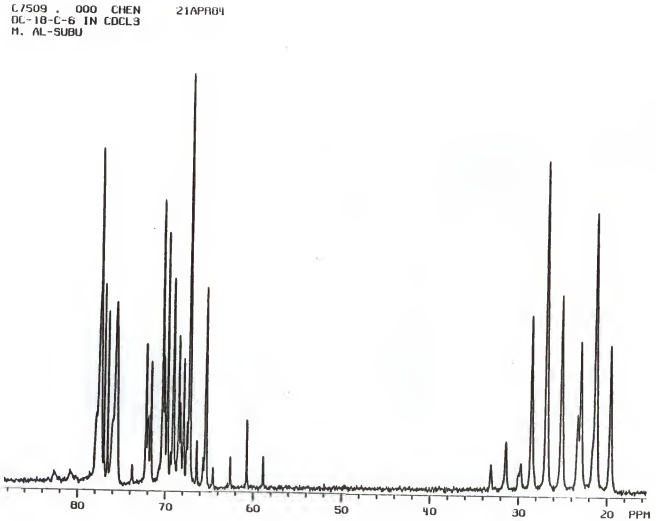
A 1.5 g sample of dibenzo-18-crown-6 ether (mp 162-164°C) was placed in a 100 mL round-bottom flask containing a teflon coated magnetic stirring bar and 30 mL of dry acetonitrile added. The mixture was stirred with gentle heating (30-40°C) until all the solid had dissolved. The solution was stored in the refrigerator (0°C) for 24 hr. The white, needle-like crystals were separated by filtration, washed, and dried under nitrogen. The product melted at 163-164°C.

The IR spectrum (Figure 4.14) of the isolated solid is missing the peaks at 3400 cm^{-1} and 2240 cm^{-1} associated with hydrogen bonds and the nitrile group, respectively. The spectrum is identical with that of pure dibenzo-18-crown-6 ether.[117]

Discussion and Conclusions

One of the two main purposes of this work was to study the formation and to characterize the adducts of the 18-crown-6 and some other crown ethers with acetonitrile. We have shown that 18-crown-6 and

Figure 4.11. Proton noise undecoupled 300 MHz ^{13}C NMR spectrum of dicyclohexyl-18-crown-6 ether in $CDCl_3$ solution.


C7509 . 000 CHEN 21APR04
DC-18-C-6 IN CDCL3
M. AL-SUBU
80
70
60
50
40
30
20
PPM

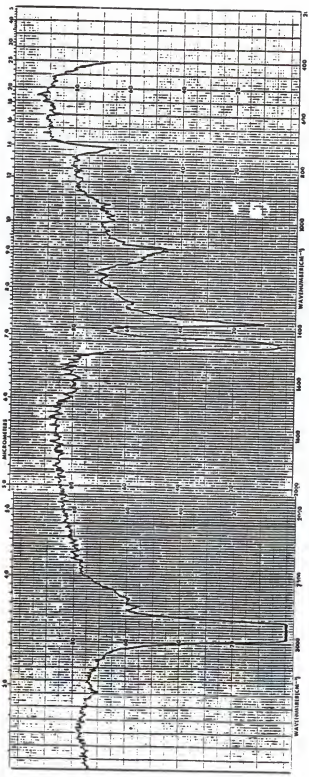
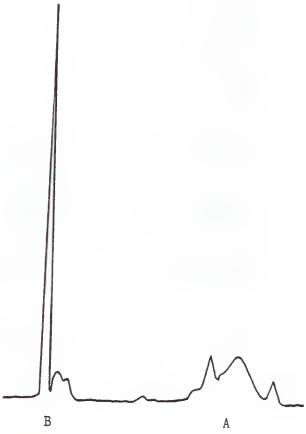


Figure 4.12. Infrared spectrum of acetonitrile-freed dicyclohexyl-18-1crown-6 ether.



Figre 4.13. The 60 MHz ^{1}H NMR spectrum of acetonitrile-freed dicyclohexyl-18-crown-6 ether in $CDCl_3$ solution.

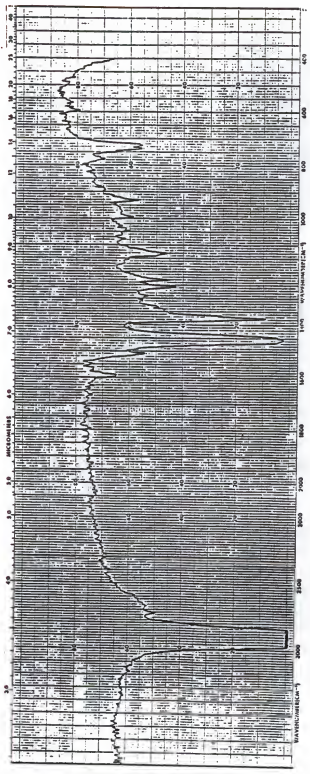


Figure 4.14. Infrared spectrum of dibenzo-18-crown-6 ether isolated from acetonitrile.

dicyclohexyl-18-crown-6 ethers react with acetonitrile to produce fairly stable complexes which contain 2 mol of acetonitrile per mole of the crown ether. This is indicated by the analytical data. The two complexes show medium to weak absorptions at about 2240 cm^{-1}, a characteristic absorption of the C≡N linkage in aliphatic nitriles. The bands assigned to vibrations of the crown ether have similar frequencies to those of the uncomplexed crown. This was also found in the Raman spectra of similar complexes.[119] Further proof of the composition of the complexes is provided by the nuclear magnetic resonance data which are shown in Table 4.2. The ^{1}H NMR spectra of the complexes (Figures 1.4 and 1.8) show the protons of the methyl group of acetonitrile as a sharp peak at about δ 2.01. The ratios of the areas of the proton peaks of acetonitrile to those for the protons of 18-crown-6 and those of dicyclohexyl-18-crown-6 ethers are 1:4 and about 1:6, respectively. The ^{13}C NMR spectra (Figures 4.5 and 4.10) show two peaks for acetonitrile: The first peak is a quartet and is in the range of δ 1.50-1.80, and the second peak is a singlet at about δ 116.30. These are assigned to the methyl group and the nitrile carbons, respectively.

The IR and NMR data suggest a high symmetry in the complexes, probably D3d where the six oxygen atoms of the crown ether form a planar ring with the two molecules of acetonitrile, one above and the other below the plane of the ring. A similar type of structure has been mentioned for similar complexes of 18-crown-6 ether with polar organic molecules such as malonitrile[136] and nitromethane.[137]

We believe that the forces by which these complexes are held together are hydrogen bonds between the slightly positive methyl hydrogens of acetonitrile molecules and the crown ether oxygen atoms

(C-H•••O) as indicated by the presence of the absorptions at about 3400 cm^{-1} in their infrared spectra. The six oxygen atoms of the crown ether are coplanar; the oxygen atom lone pairs and the two O-C bonds form a tetrahedral environment around the oxygen atom. In theory, several orientations of the oxygen lone pairs--with respect to the hydrogen of acetonitrile--could form stable hydrogen bonds. However, for D_{3d} symmetry, the most stable structure would be the one in which the hydrogen atom is trigonally oriented with two lone pairs of two neighboring oxygen atoms of the ring.

Dibenzo-18-crown-6 ether does not form a complex with acetonitrile as indicated by the melting point and the infrared spectrum of the isolated solid (Figure 4.14) which are identical with those of pure dibenzo-18-crown-6 ether. The failure of dibenzo-18-crown-6 ether to form such a complex with acetonitrile can be explained by the reduced electron density at the oxygen atoms resulting from the electron attracting substituents--benzo units--which produce a marked drop in the binding capacity of the crown ether.

The other principal purpose of this study was to determine the possibility of utilizing acetonitrile to separate a mixture of isomers of dicyclohexyl-18-crown-6 ether, namely, cis-syn-cis (IA) and cis-anti-cis (IB) isomers. We have found in this work that there is a marked difference in the complexing ability of these two isomers toward acetonitrile. This is indicated by the formation of a complex with the cis-anti-cis isomer but not with the cis-syn-cis isomer. Since the nuclearmagnetic resonance evidence on the conformation of the two isomers is not conclusive, the melting point measurements is the next main method--after x-ray--to differentiate between the two isomers (IA mp 59-60°C, lit 61-62°C;

IB mp 68-69°C, lit 69-70°C]. The infrared spectrum of the acetonitrile-freed dicyclohexyl-18-crown-6 ether (IB) in Figure 4.12 is in agreement with that reported by Pederson.[117]

Though it was not the purpose of this study to analyze the ^{13}C NMR spectrum of dicyclohexyl-18-crown-6 ether, it was noticed that the ^{13}C NMR spectrum of the dicyclohexyl-18-crown-6 ether-acetonitrile complex (Figure 4.10) has a smaller number of peaks and looks more resolved than that of dicyclohexyl-18-crown-6 ether (Figure 4.11), especially in the region between δ 60 and δ 75. This might be explained by conformational changes for uncomplexed and complexed dicyclo-18-crown-6 ether as follows: In the uncomplexed ether, the cavity surrounded by the six oxygen atoms is elliptical in shape[138] which allows more interaction between the carbon atoms and the hydrogens of the crown ether. In the complexed crown ether, we believe, as was mentioned earlier, that the oxygen atoms are planar, and all point toward the hydrogen atoms of acetonitrile in the cavity of the ether making the complex more symmetrical than the uncomplexed ether. Similar conformational changes for uncomplexed and complexed dibenzo-18-crown-6 were reported.[139]

Although the difference in the stability of the complexes of the two isomers of dicyclohexyl-18-crown-6 ether, IA and IB, with several metal ions was reported to follow the order of IA > IB,[123] we found the opposite order in the binding ability of the two isomers toward acetonitrile. This behavior could be explained by the fact that in the cases reported, the complexation was between the crown ether and metal ions. The metal ions can be described as charged spheres capable of bonding by electrostatic interaction with a source of a negative charge and with no directional restrictions imposed on the bonds from the metal. In our

case, as mentioned before, the forces between acetonitrile and the crown ether are hydrogen bonds. Therefore, for strong complexations, the location of the binding sites must allow a "tripod" hydrogen bond arrangement. Bearing in mind that there are two acetonitrile molecules per one molecule of the crown ether in the complex (above and below), this means that steric hindrance plays an important rule in the complexation ability. In the cis-anti-cis isomer IB, the steric hindrance resulting from the four bridgehead hydrogens is divided equally above and below the plane of the ring, compared with the other isomer IA in which the steric hindrance is all above or below the plane of the ring. This results in a higher binding ability of IB than that of IA.

Summary

Elemental analyses, proton and carbon-13 NMR, and infrared data reported herein confirm the fact that 18-crown-6 and dicyclohexyl-18-crown-6 ethers react with acetonitrile to form complexes of the type crown ether•2 acetonitrile. It is postulated that the six oxygen atoms of the complexed crown ether are in one plane and that the two acetonitrile molecules are one above and one below the plane with approximately D3d geometry. The forces that hold the complex together are believed to be hydrogen bonds between the hydrogen atoms of acetonitrile and the oxygen atoms of the crown ether in such a way that maximum stability is obtained.

The failure of dibenzo-18-crown-6 ether to form a complex with acetonitrile is explained by the low basicity of the oxygen atoms resulting from electron withdrawing properties of the two benzo units.

It is also shown from the melting points and the infrared data that of the two isomers, cis-syn-cis (IA) and cis-anti-cis (IB) dicyclohexyl-18-crown-6 ether, only the second isomer IB can form a stable complex with acetonitrile. This was explained by less steric hindrance in the final structure of the resulting complex of IB and acetonitrile. This different behavior of the two isomers of dicyclohexyl-18-crown-6 ether toward acetonitrile may be used as a basis for a new technique which take advantage of the difference in binding ability of the two isomers toward acetonitrile to separate a mixture of the two isomers. This technique may be better than presently reported methods which are expensive and time consuming.

CHAPTER FIVE

CONCLUSIONS

The reactions of dinitrogen tetroxide with some crown ethers and other alicyclic nitrogen, oxygen, and sulfur bases have been examined and the products from each of the reactions identified. The reaction with 1,4-thioxane results in the oxidation of the sulfur atom to yield 1,4-thioxane 4-oxide. The reactions of dinitrogen tetroxide with the tertiary amines N-methylmorpholine, N,N'-dimethylpiperazine, and triethylenediamine result in the oxidation of the amine to the amine N-oxide or the amine N,N'-dioxide. However, the large dipole moment of the N^+-O^- bond causes the resulting amine oxides to react further with dinitrogen tetroxide to give adducts in which the ratio of the amine oxide to dinitrogen tetroxide is 2:1 or 1:1 depending on the number of N^+-O^- bonds per molecule of the amine oxide. These adducts appear to be complexes of ionic nitrosyl nitrate rather than molecular adducts.

Aliphatic crown ethers form adducts with dinitrogen tetroxide in which the ratio of the crown ether to dinitrogen tetroxide is 1:1 for the ethers with a large cavity size (6 or 8 oxygen atoms) and 2:1 for those with smaller cavities (4 or 5 oxygen atoms). These adducts also appear to be complexes of ionic nitrosyl nitrate. The reactions of dinitrogen tetroxide with dibenzo-18-crown-6 ether result in the nitration of the two benzo units to give the dinitro derivative and only in one isomeric form, the cis-isomer.

The reactions of chloramine with diallyl- and triallylamines yield 2,2-diallyltriazanium chloride and 1,1,1-triallylhydrazinium chloride, respectively. The 2,2-diallyltriazanium chloride undergoes a radical initiated polymerization to yield a cross-linked polymer which is insoluble in a wide variety of solvents. The formation of the polymer as a cross-linked rather than a cyclopolymer results from the reppulsion between the unshared pair of electrons on the amino nitrogen and the odd electron produced on the -carbon by the initiator.

It has been found that when the reaction of chloramine with 1,1-dimethylhydrazine is carried out in the presence of a catalytic amount of 18-crown-6 ether, both the yield and purity of the 2,2-dimethyltriazanium chloride are improved. An S_N2-type mechanism to explain the action of 18-crown-6 ether on the chloramination of 1,1-dimethylhydrazine to produce 2,2-dimethyltriazanium chloride is proposed.

A solid adduct is formed between 18-crown-6 ether and a chloramine solution in diethyl ether. The structure of the adduct is believed to involve hydrogen bonding between the chloramine molecule and the oxygen atoms of the crown ether. The chloramine-18-crown-6 ether adduct acts as a chloraminating agent toward triethylamine.

The 18-crown-6 and dicyclohexyl-18-crown-6 ethers react with acetonitrile to form complexes containing two moles of acetonitrile per mole of the crown ether. It is believed that the six oxygen atoms of the crown ether are in one plane and that the two acetonitrile molecules are above and below the plane, respectively, with approximately D_{3d} geometry.

REFERENCES

1. Sisler, H. H., J. Chem. Ed., 34, 555 (1957).
2. Broadly, J. S., and Robertson, J. M., Nature, 164, 915 (1949).
3. Smith, D. W., and Hedberg, K., J. Chem. Phys., 25, 1282 (1956).
4. Groth, P., Acta Chem. Scand., 17, 2419 (1963).
5. Cartwright, B. S., and Robertson, J. M., Chem. Commun., 82 (1966).
6. McClelland, B. W., Gundersen, G., and Hedberg, K., J. Chem. Phys., 56, 4541 (1972).
7. Bent, H. A., Inorg. Chem., 2, 747 (1963).
8. Novick, S. E., Howard, B. J., and Klemperer, W., J. Chem. Phys., 57, 5619 (1972).
9. Pauling, L., "The Nature of Chemical Bond," Cornell University Press: Ithaca, New York, 1960, p. 349.
10. Ahlrichs, R., and Keil, F., JACS, 7615 (1974).
11. Redmond, T. F., and Wayland, B., J. Phys. Chem., 72, 1626 (1968).
12. Clusius, K., and Vecchi, M., Helv. Chim. Acta, 36, 930 (1953).
13. Sisler, H. H., "Chemistry in Non-Aqueous Solvents," Chapman and Hall, Ltd.: London, 1961, pp. 65-83.
14. Addison, C. C., and Hodge, N., J. Chem. Soc., 2987 (1961).
15. Addison, C. C., and Simpson, W. B., J. Chem. Soc. (A) (1961).
16. Sei Otsuka, Nakamura, A., Tatsuno, Y., and Miki, M., JACS, 94, 3761 (1972).
17. Levison, J. J., and Robinson, S. D., J. Chem. Soc. (A), 762 (1971).
18 Kubota, M., Koerntgen, C. A., and McDonald, G. W., Inorg. Chim. Acta, 30, 11a (1978).
19. Addison, C. C., and Conduit, C. P., J. Chem. Soc., 1390 (1952).

20. Addison, C. C., Conduit, C. P., and Thompson, R., J. Chem. Soc., 1303 (1952).

21. Addison, C. C., Hodge, N., and Sheldon, J. C., Chemistry and Industry, 1338 (1953).

22. Addison, C. C., and Lewis, J., Quart. Revs. (London), 9, 115 (1955).

23. Gibbins, B. J., Eichhorn, G. L., and Sisler, H. H., JACS, 76, 4668 (1954).

24. Ling, H. W., Sisler, H. H., and Schechter, H., JACS, 74, 877 (1952).

25. Rubin, B., Sisler, H. H., and Schechter, H., JACS, 75, 5158 (1953).

26. Whanger, J. G., and Sisler, H. H., JACS, 75, 5158 (1953).

27. Comyns, A. E., Nature, 172, 491 (1953).

28. Comyns, A. E., J. Chem. Soc., 1557 (1955).

29. Davenport, D. A., Burkhardt, H. J., and Sisler, H. H., JACS, 75, 4175 (1953).

30. Addison, C. C., and Sheldon, C., J. Chem. Soc., 2705 (1956).

31. Horner, Von L., and Hubenett, F., Ann., 597, 193 (1953).

32. Whitaker, R. D., and Sisler, H. H., J. Org. Chem., 25, 1038 (1960).

33. Leonard, N. J., and Johnson, C. R., J. Org. Chem., 27, 283 (1962).

34. Millen, D. J., J. Chem. Soc., 2600 (1950).

35. Reid, E. E., "Organic Chemistry of Bivalent Sulfur," Vol. II, Chemical Publishing Co., Inc.: New York, 1960, p. 64.

36. Szare, W. A., Vyas, D. M., Sepulchre, A. M., Gevo, S. D., and Lukacs, G., Can. J. Chem., 52, 2041 (1974).

37. Frieze, D. M., and Evans., S. A., J. Org. Chem., 40, 2690 (1975).

38. Reeder, F., and Wilso, D. L., Brit. Patent 1,006,600 (1965).

39. Martin, D. J., U.S. Patent 3,641,054 (1972).

40. Meisenheimer, J., Ber., 41, 3966 (1908).

41. Meisenheimer, J., Ann., 385, 117 (1911).

42. Meisenheimer, J., Ann., 428, 252 (1922).

43. Meisenheimer, J., Glawe, H., Greeske, H., Shchorning, A., and Vieweg, E., Ann., 449, 191 (1926).

44. Feigenbaum, W. H., and Michel, R. H., J. Polymer Sci. A-1, 9, 817 (1971).

45. Shchori, E., Jagur-Grodzinski, J., and Shporer, M., JACS, 95, 3842 (1973).

46. Shchori, E., and Jagur-Grodzinski, J. J., Appl. Polymer Sci., 20, 1665 (1976).

47. Shchori, E., and Jagur-Grodzinski, J. J., Appl. Polymer Sci., 20, 773 (1976).

48. Kime, D. E., and Norymberski, J. K. J. Chem. Soc. Perkin, 1, 1048 (1977).

49. Raschig, F., Ber., 40, 4586 (1907).

50. Mattair, R., and Sisler, H. H., JACS, 73, 1619 (1951).

51. Sisler, H. H., Neth, F. T., Drago, R. J., and Yaney, D., JACS, 76, 3906 (1954).

52. Sisler, H. H., and Weiss, J., Inorg. Chem., 4, 1514 (1965).

53. Prakash, H., and Sisler, H. H., Allgem. u. prakt. Chem., 4, 123 (1970).

54. Hart, W. A., and Sisler, H. H., Inorg. Chem., 3, 617 (1964).

55. Edwards, J. O., and Pearson, R. G., JACS, 84, 16 (1962).

56. Pearson, R. G., Sobel, J., and Songstad, J., JACS, 90, 319 (1968).

57. Kren, R. M., and Sisler, H. H., Inorg. Chem., 9, 836 (1970).

58. Sisler, H. H., Neth, F. T., and Hurley, F. R., JACS, 76, 3909 (1954).

59. Utvary, K., and Sisler, H. H., Inorg. Chem., 5, 1835 (1966).

60. Utvary, K., and Sisler, H. H., Inorg. Chem., 7, 698 (1968).

61. Giordano, T. J., and Sisler, H. H., Inorg. Chem., 16, 2043 (1977).

62. Sisler, H. H., Mathur, M. A., Jain, S. R., Ind. Eng. Chem. Prod. Res. Dev., 20, 183 (1981).

63. Sisler, H. H., Kren, r. M., and Utvary, K., Inorg. Chem., 8, 2007 (1969).

64. Omietanski, G. M., and Sisler, H. H., JACS, 78, 1211 (1956).

65. Giordano, T. J., Palenik, G. J., and Sisler, H. H., Inorg. Chem., 15, 751 (1976).

66. Mathur, M. A., Sisler, H. H., and Morgenthaler, L. N., Inorg. Chem., 2350 (1979).

67. Omietanski, G. M., Kelmers, A. D., Shellman, R. W., and Sisler, H. H., JACS, 78, 3874 (1956).

68. Jain, S. R., Mathur, M. A., and Sisler, H. H., Inorg. Chem., 19, 2192 (1980).

69. Sisler, H. H., Sarkis, A., Ahuja, H. S., Drago, R. J., and Smith, N. L., JACS, 81, 2982 (1959).

70. Sisler, H. H., Ahuja, H. S., and Smith, N. L., Inorg. Chem., 1, 84 (1962).

71. Sisler, H. H., and Frazier, S. E., Inorg. Chem., 4, 1204 (1965).

72. Sisler, H. H., Gilson, I. T., Inorg. Chem., 4, 273 (1965).

73. Sisler, H. H., Frazier, S. E., Rice, R. G., and Sanchez, M. G., Inorg. Chem., 5, 326 (1966).

74. Highsmith, R. E., and Sisler, H. H., Inorg. Chem., 7, 1740 (1968).

75. Sisler, H. H. and Frazier, S. E., Inorg. Chem., 11, 1431 (1972).

76. Sisler, H. H., and Jain, S. R., Inorg. Chem., 8, 1243 (1969).

77. Sisler, H. H., and Frazier, S. E., Inorg. Chem., 5, 925 (1966).

78. Sisler, H. H., and Smith, N. L., J. Org. Chem., 26, 4733 (1961).

79. Clemens, D. F., and Sisler, H. H., Inorg. Chem., 4, 1222 (1965).

80. Jain, S. R., Krannich, L. K., Highsmith, R. E., and Sisler, H. H., Inorg. Chem. 6, 1058 (1967).

81. Jain, S. R., Brey, W. S. Jr., and Sisler, H. H., Inorg. Chem., 6, 515 (1967).

82. Denney, D. B., and Felton, S. M., Inorg. Chem., 7, 99 (1968).

83. Nielsen, R. P., Vincent, J. F., and Sisler, H. H., Inorg. Chem., 2, 760 (1963).

84. Kanamueller, J. M., and Sisler, H. H., Inorg. Chem., 6, 1765 (1967).

85. Sisler, H. H., and Jain, S. R., Inorg. Chem., 7, 105 (1968).

86. Krannich, L. K., and Sisler, H. H., Inorg. Chem., 8, 1032 (1969).

87. Sisler, H. H. and Stratton, C., Inorg. Chem., 5, 2003 (1966).

88. Krannich, L. K., and Sisler, H. H., Inorg. Chem., 11, 1226 (1972).

89. Krannich, L. K., Thewalt, U., Cook, W. J., Jain, S. R., and Sisler, H. H., Inorg. Chem., 12, 2204 (1973).

90. McKenney, R. L., and Sisler, H. H., Inorg. Chem., 6, 1178 (1967).

91. Sisler, H. H., Kotia, N. K., and Highsmith, R. E., J. Org. Chem., 35 1742 (1970).

92. Sisler, H. H., and Kotia, N. K., J. Org. Chem., 36, 1700 (1971).

93. Prakash, H., and Sisler, H. H., J. Org. Chem., 35, 3111 (1970).

94. Ogata, Y., Izawa, Y., and Tomioka, H., Tetrahedron., 23, 1509 (1967).

95. Abraham, R. J., and Loftus, P., "Proton and Carbon-13 NMR Spectroscopy," Heyden: London, 1980, p. 29.

96. Butler, G. B., and Bunch, R. L., JACS, 71, 3120 (1949).

97. Butler, B. B., "The Chemistry and Properties of Poly(diallyl ammonium salts)," presented at the International Symposium on Polymeric Amines and Ammonium Salts, Ghent, Belgium, 24-26 September 1979/E. J. Goethals, ed., Pergamon Press: Oxford, New York, 1980.

98. Gösl, R., Angew. Chem. Intern. Ed. Engl., 1, 405 (1962).

99. Utvary, K., Monatsh. Chem., 99, 1473 (1968).

100. Utvary, K., Monatsh. Chem., 99, 1483 (1968).

101. Utvary, K., Monatsh. Chem., 99, 2321 (1968).

102. Utvary, K., Sisler, H. H., and Kitzmantel, P., Monatsch. Chem., 100, 401 (1969).

103. Londini, D., Montanari, F., and Pivisi, F. M., Chem. Commun., 879 (1974).

104. Makosza, M., and Ludwikow, M., Angew. Chem., 86, 744 (1974).

105. Makosza, M., and Ludwikow, M., Angew. Chem. Intern. Ed., 13, 665 (1974).

106. Smith, S. G., and Hanson, M. P., J. Org. Chem., 36, 1931 (1971).

107. Akabori, S., Ohtomi, M., and Arai, K., Bull. Chem. Soc. Japan, 49, 746 (1976)

108. Nakabayashi, T., Kawamura, S., Horrii, T., and Hamada, M., Chem. Lett., 869 (1976).

109. Hiraoka, M., "Crown Compounds," Elsevier Scientific Publishing Company: Amsterdam, 1982, p. 183.

110. Highsmith, r. E., and Sisler, H. H., Inorg. Chem., 5, 1029 (1969).

111. Schmitz, E., Schramm, S., and Simon, H., Angew. Chem. Intern. Ed. Engl., 5, 578 (1966).

112. Translated from Izvestya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, August 1981, pp. 1735-1739.

113. Berg, A., Ann. Chim. Phys., 3, 319 (1894).

114. Charles, B. C., "Developments in Inorganic Nitrogen Chemistry," Vol. 2, Chapter 3, Elselvier Scientific Publishing Co.: New York, 1973, p. 77.

115. Pedersen, C. J., J. Org. Chem., 36, 1960 (1971).

116. Pedersen, C. J., JACS, 89, 2495 (1967).

117. Pedersen, C. J., JACS, 89, 7017 (1967).

118. Gokel, G. W., Cram, D. J., Liotta, C. L., Harris, H. P., and Cook, F. L., J. Org. Chem., 39, 2445 (1974).

119. McLachlan, R. G., Spectrochim. Acta A, 30, 2153 (1974).

120. Pedersen, C. J., Org. Synth., 52, 66 (1972).

121. Frensdorff, H. K., JACS, 93, 600 (1971).

122. Izatt, R. M., Haymore, B. L., Bradshaw, J. S., and Christensen, J. J., Inorg. Chem., 14, 3132 (1975).

123. Burdern, I. J., Coxon, A. C., Stoddart, J. F., and Wheatley, C. M., J. Chem. Soc. Parkin Trans., 1, 220 (1977).

124. Newkome, G. R., Sauer, J. D., Roper, J. M., and Hager, D. C., Chem. Rev., 77, 513 (1977).

125. Pedersen, C. J., JACS, 92, 391 (1970).

126. Pedersen, C. J., JACS, 89, 386 (1970).

127. Pedersen, C. J., and Frensdorff, H. K., Angew. Chem. Intern. Ed., 11, 16 (1972).

128. Pedersen, C. J., and Frensdorff, H. K., Angew. Chem., 84, 16 (1972).

129. Pedersen, C. J., and Frensdorff, H. K., Angew. Chem. Intern. Ed., 11, 1, (1972).

130. Knipe, A. C., J. Chem. Ed., 53, 618 (1976).

131. Poonia, N. S., Chem. Rev., 79, 389 (1979).

132. Dye, J. L., Angew. Chem. Intern. Ed., 18, 587 (1980).

133. Bellamy, L. J., "Advances in Infrared Group Frequencies," Chapter 8, Chapman and Hall: London, 1975.

134. Smith, A. L., "Applied Infrared Spectroscopy," Appendix 2, Wiley: New York, 1979.

135. Nuclear Magnetic Resonance Spectra, Sadtler Research Laboratories, Vol. 23, 1976.

136. Kaufmann, R., Knöchel, A., Kopf, J., Oehler, J., and Rudolph, G., Chem. Ber., 110, 2249 (1977).

137. Unpublished work, quoted in ref. 119

138. Dalley, N. K., Smith, D. E., Izatt, R. M., and Christensen, J. J., J. Chem. Soc. Chem. Comm., 90 (1972).

139. Bright, D., and Truter, M. R., J. Chem. Soc. (B), 1544 (1970).

BIOGRAPHICAL SKETCH

Mohammed Mahmoud Al-Subu was born July 17, 1954, in Seilet Elharthieh, West Bank of Jordan. In June 1973 he graduated from Jenin High School, Jenin, West Bank. Upon graduation he began his college education at the University of Jordan in Amman, Jordan. He received the degree of Bachelor of Science from the University of Jordan in February 1977. At this time he enrolled in the Graduate School of the same university and received the degree of Master of Science in June 1979. From September 1979 until July 1980 he worked as an instructor in the Department of Chemistry at An-Najah National University, Nablus, West Bank. In September 1980 he enrolled in the Graduate School of the University of Florida. He worked as a teaching assistant while pursuing his graduate degree.

Mr. All-Subu is married to the former Amal M. Jaradat and is the father of two children, Awni and Mahmoud.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Harry H. Sisler, Chairman
Distinguished Service Professor
of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Francis E. Dunnam
Professor of Physics

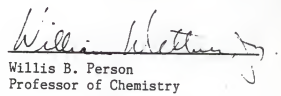
I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

George B. Butler
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

George E. Ryschkewitsch
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



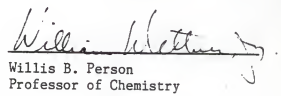
Willis B. Person
Professor of Chemistry

This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate Council, and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

December 1984

Dean for Graduate Studies and Research

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



Willis B. Person
Professor of Chemistry

This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate Council, and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

December 1984

Dean for Graduate Studies and Research